Desulfurization of Gasoline and Diesel Fuels, Using Non-Hydrogen Consuming Techniques.

Abdullah Al-Malki

Master of Science

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King Fahad University of Petroleum and Minerals

Chemistry Department

CHAPTER 1

INTRODUCTION

Crude oil is the largest and most widely used source of energy in the world. Major portions of the crude oils are used as transportation fuels such as gasoline, diesel and jet fuel. However, such crudes contain sulfur, typically in the form of organic sulfur compounds. The sulfur content and the API gravity are two properties which have a great influence on the value of the crude oil. The sulfur content is expressed as a percentage of sulfur by weight and varies from less than 0.1% to greater than 5% depending on the type and source of crude oils [1]. Sulfur compounds exist in various forms and can be classified into four main groups: mercaptans, sulfides, disulfides and thiophenes. It is well known that the sulfur compounds are undesirable in refining process as they tend to deactivate some catalysts used in crude oil processing. Sulfur compounds can cause several corrosion problems in pipeline, pumping, and refining equipment, as well as the premature failure of combustion engines and poisoning of the catalytic converters that are used in automotive engines. Today, the strongest motivation for the reduction of sulfur in fuels is due to environmental regulation which is imposing stringent limits for sulfur levels in transportation fuels. Sulfur is responsible for the emission of sulfur oxides (SOx) resulting from the combustion of fuels used in transportation. High sulfur content is also responsible for the particulate emissions from trucks and buses. It also precludes the use of advanced after treatment systems which cannot work with such high sulfur content.

LITERATURE REVIEW

Removing organic sulfur from hydrocarbon fuels is becoming an increasingly challenging task for refineries. This is due to the stringent environmental regulations which are placing considerable pressure on refinery operators to reduce sulfur below 10 ppm by the year 2010 [2] (figure 1). The current specification in Europe and the USA calls for a maximum sulfur content of 50 ppm in gasoline and diesel by 2005 [2-3]. Sulfur compounds are present in crude oil in a wide range of both aliphatic and aromatic forms and mainly concentrated in the heavy part of the crude oil [4-5]. To meet the demand for gasoline, catalytic cracking processes are employed industrially to convert these heavy low value heavy cuts to products of high value. During these processes, major sulfur compounds are removed by conventional hydrodesulphurization (HDS) catalytic processes [5]. However, the catalysts are not active in removing refractory sulfur-compounds that are sterically hindered. This is particularly true in the case of sulfur compounds like thiophenes and multi ring aromatic sulfur compounds, such as dibenzothiophene (DBT) and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT). In order to meet future fuel specifications, such sulfur-compounds must be removed or reduced to target limits within a regulatory period. Much effort has been devoted to developing techniques that can reduce or remove such refractory sulfur compounds by oxidation/extraction and biodesulfurization [7-16]. In general, diesel fuel and gasoline contain 20 to 30 percent aromatics but less than 1 percent sulfur, so removing the sulfur without removing the aromatics is difficult, particularly in the HDS process which also

potentially hydrogenates (saturates) aromatics. It is preferable however, to include certain aromatic compounds such as toluene and naphthalene in the fuel as they contribute significantly to fuel quality [10-14].

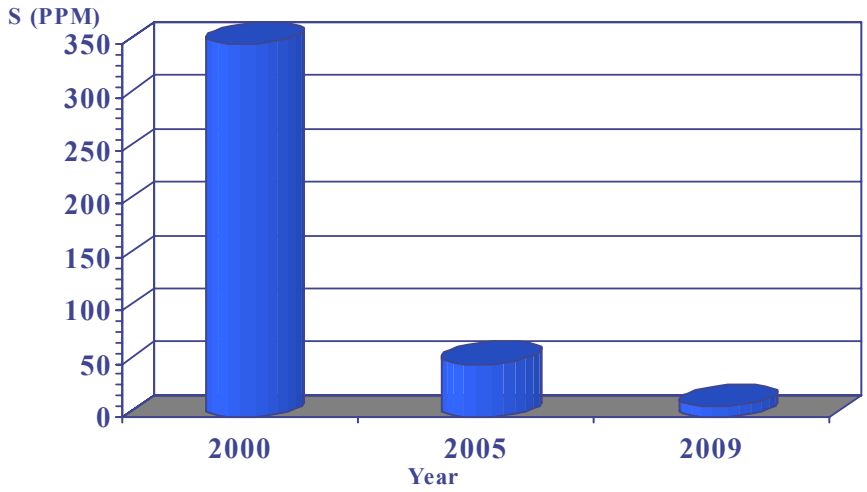


Figure 1. Euro III sulfur limit (ppm) for diesel (2000)

1.1 CURRENT PROCESS FOR DESULFURIZATION

Heavy hydrocarbon feedstocks that undergo catalytic refining processes generate products, such as gasoline and diesel with large amounts of sulfur-containing organic compounds [1]. The products containing sulfur compounds are usually hydrodesulfurized through several processes using well-established catalyst systems. The associated organic sulfur compounds exist in several forms such as mercaptans, aliphatic and cyclic thioethers and thiophenes and their derivatives. There are two approaches used to reduce sulfur level in petroleum refining business: conventional hydrodesulfurization and non-hydrogen consuming desulfurization

1.1.1 Conventional hydrodesulfurization (HDS).

Conventional hydrodesulfurization (HDS) with Mo, Ni or W-based catalysts are widely used to reduce sulfur content. Mercaptans, thioethers, and disulfides, for example, can be removed relatively easy using this process. Other sulfur-bearing organic compounds such as aromatic, cyclic, and condensed multicyclic compounds are more difficult to remove [15]. Thiophene, benzothiophene, dibenzothiophene, other condensed-ring thiophenes, and substituted forms of these compounds are particularly difficult to remove by hydrodesulfurization. Typically, the hydrodesulfurization process involves catalytic treatment with hydrogen to convert the various sulfur compounds to hydrogen sulfide [16-17]. The kinetics investigation into the behavior of 4,6-alkyldibenzothiophene (4,6-DADBT) led to two contradictory explanations. First, the transformation of 4,6-DADBT is limited by the adsorption step via sulfur atom. The second hypothesis suggests that the adsorption occurs through π-electrons of the aromatic system [8]. In general, the reaction mechanism of DBT and 4,6-DMDBT through HDS process was suggested to proceed via two main pathways (Figure 2). One is a direct desulfurization pathway where sulfur is removed without affecting the aromatic rings. The other is via a hydrogenation pathway, in which aromatic rings of DBT compounds are preferentially hydrogenated to 4H- or 6H-DBT intermediates and are subsequently desulfurized [16]. Thus, the desulfurization rate of hindered compounds is greatly increased through the hydrogenation route. Without one or both of the rings, the molecule is much more flexible and the sulfur atom can approach the catalyst surface much more easily. However, the “hard sulfur compounds” like benzothiophenes and its derivatives are the most sterically

hindered compounds that have been identified in diesel fractions after conventional hydrodesulfurization (HDS) ranging in concentration from 0.2-0.3 wt.%. This would indicate that these catalysts are not efficient enough to desulfurize the most refractory sulfur-containing compounds e.g. DBT and its derivatives [16-17]. However, the HDS is limited in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs),especially DBTs having alkyl substituents on 4 and/or 6 positions. The production of light oil, with very low levels of sulfur-containing compounds, therefore requires inevitably the application of severe operating conditions and the use of especially active catalysts [18-20]

HDS is a commercially proven refining process that passes a mixture of heated feedstock and hydrogen over catalysts to remove sulfur. Refineries can desulfurize distillate streams by hydrotreating the straight run streams that generated from direct distillation of crude oil, hydrotreating streams coming out from conversion units such as fluid catalytic cracking (FCC) and hydrocracker units.

By controlling the hydrotreating conditions and selecting the appropriate catalysts, refineries may meet the ultra low sulfur diesel (ULSD) on fuels that are produced from straight runs streams. The difficulty however, arises in the desulfurization of other steams that come from the conversion units, which mostly include the refractory sulfur compounds. Meeting the sulfur requirement for gasoline is believed to be the greatest challenge for the refining business requiring substantial revamps to equipment or even construction of new units. This is due to the fact that most of the gasoline production in the market today is coming from

cracked stocks that contain a larger concentration of compounds with aromatic rings and high olefin content, thus making sulfur removal more difficult. The need to desulfurize the cracked stocks in addition to the straight-run streams will direct the refiners to choose the most cost-effective technology [16-21].

In essence, refiners must desulfurize all diesel-blending components in order to meet the 10 ppm ULSD specification that will take effect from 2009. In the case of diesel, a two-stage deep desulfurization process will most probably be sufficient to meet the 10 ppm sulfur target. The first stage can reduce the sulfur level to below 250 ppm with a second stage that could produce diesel product with 10 ppm sulfur or less. In some cases the first stage could be a conventional hydrotreating unit with moderate adjustments to the operating parameters. The second stage would require substantial modification of the desulfurization process, primarily through use of higher pressure, increasing hydrogen flow rate and purity, reducing space velocity, and choice of catalyst. Such operational requirements to deep desulfurize cracked stocks also need a higher reactor pressure [5&21].

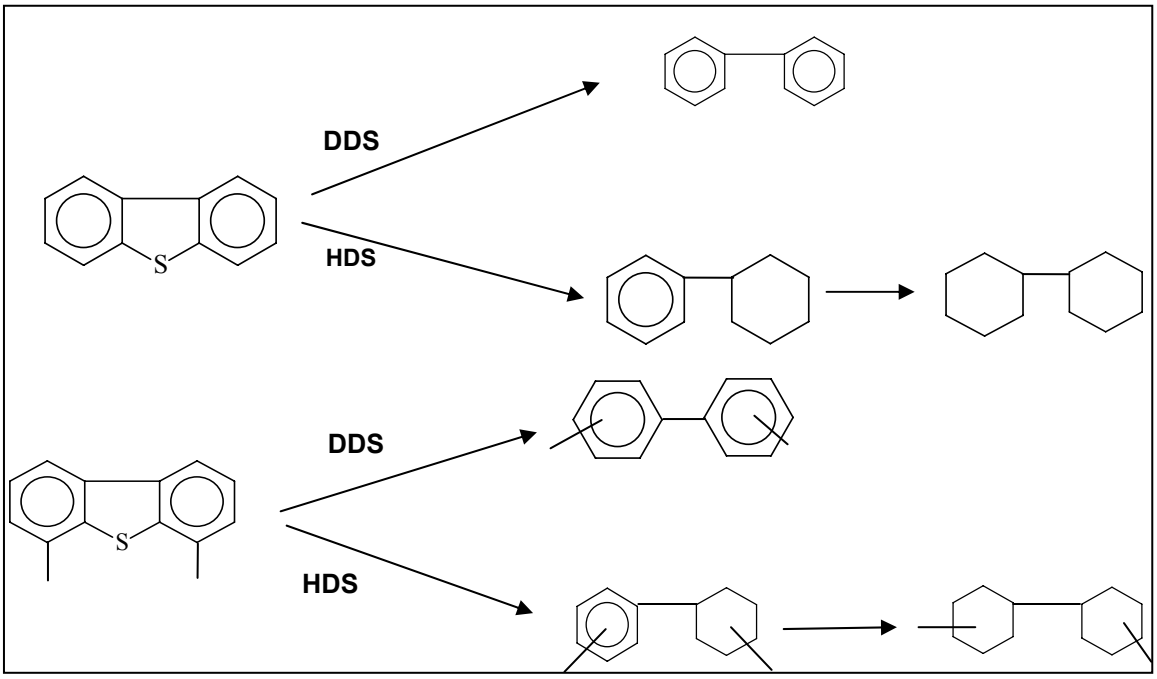


Figure 2. Direct Desulfurization and Hydrogenation Pathways for Hydrodesulfurization of Benzothiophenes

1.1.2 The non-hydrogen consuming desulfurization

The non-hydrogen consuming desulfurization studies can be categorized in four techniques: biodesulfurization, oxidative/extraction, C-S insertion using homogeneous catalyst and physical separation [21&22]. The biodesulfurization approach has progressed significantly and it has a potential to be implemented on a larger scale. The basis of this approach is to convert the sulfur organic compounds to corresponding sulfoxides or sulfones biocatalytically. An example is shown in figure 3 for converting DBT to sulfoxides, sulfones and finally to hydroxyl biphenyl [23-29]. Although, there is a lot of research going on in this area, the application of this approach is limited by the slow biodegradation process.

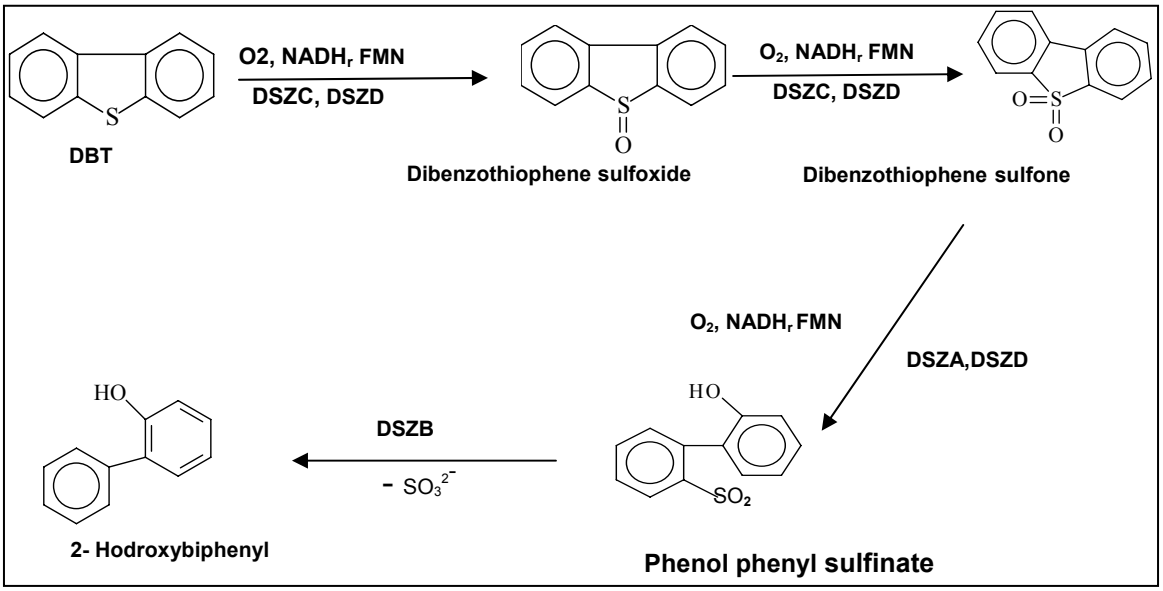


Figure 3. Biodesulfurization pathway for DBT

Oxidative desulfurization (ODS) has been given much interest as an alternative technology for deep desulfuriztion. The ODS is basically a two-stage process; oxidation, followed by liquid extraction. This was first introduced by Guth and Diaz in 1974 and Guth et al. in 1975 using nitrogen dioxides as an oxidant, followed by extraction with methanol to remove both sulfur and nitrogen compounds from petroleum stocks [5&21]. Tam and Kittell described a process for purifying hydrocarbon aqueous oils containing both sulfur and nitrogen compound by first reacting the oil with an oxidizing gas containing nitrogen oxides and then extracting the with solvents in two stages [5,13,21]. The oxidation-extraction process used by Patrick et al. (1990) operates at ambient pressure and low temperature (typically 0-30^{o}C), using nitric acid or nitrogen oxides as oxidants, and any polar solvents for extraction [5,13]. In the petroleum industry, solvent extraction techniques have been used to remove sulfur and nitrogen compounds from light oil without any pretreatment of petroleum feedstocks. The solvent can be recovered and reused through a distillation process [13,21]. In general, employing

only solvent extraction of petroleum products to remove sulfur creates an associated loss of useful hydrocarbons, in addition to poor sulfur removal [5,21,30]. This is probably due to the small difference in the polarity between sulfur compounds and other aromatic hydrocarbons. Therefore, the selective oxidation approach of increasing the polarity of sulfur compounds , then removing them by selective extraction, has received much great attention recently with some success, particularly in diesel fuel. The greatest advantages of the ODS process are low reaction temperature and pressure, and removing the need for expensive hydrogen that is used in the conventional HDS process. Another feature of ODS is that the refractory sulfur compounds in ODS are easily converted by oxidation [35-34]. Therefore, ODS has great potential to be a complementary process to traditional HDS for achieving deep desulfurization [13,35-37].

In the ODS process, the sulfur-containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulfoxides and sulfones. These are preferentially extracted from light oil due to their increased relative polarity [5,11,13, 21]. Any unused oxidant that remains in the light oil can be removed by water washing and extracting. The oxidized compounds can be extracted from the light oil by using a non-miscible solvent. Depending on the solvents used for extraction, the oxidized compounds and solvent are separated from the light oil by gravity separation or centrifugation. The light oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as absorption using silica gel and aluminum oxide. The solvent is separated from the mixture of solvent and oxidized

compounds by a simple distillation for recycling and re-use. By using this process, the maximum sulfur removal is achieved with minimum impact on the fuel quality [21,22,36-38].

Many oxidants have been investigated which include peroxy organic acids, catalyzed hydroperoxides, inorganic oxidants such as inorganic peroxy acids, peroxy salts and O_3, etc [21,36].

The second step of this process is the removal of the oxidized compounds by contacting the distillate with a selective extraction solvent. As reported in the literature, the liquid-liquid extraction technique using water-soluble polar solvents (DMSO, DMF, and acetonitrile) is usually used [5,21,36-38]. The former two solvents have a high extractability for sulfones but also have a high boiling point at 573K. This is close to the boiling point of the sulfones, thus creating difficulty in separation and reuse for further extraction [5,13,21]. Yasuhiro Shiraishi et al, have used acetonitrile in their work as the extraction solvent, since it has a relatively low boiling point (355K) and can be easily separated from the sulfones by distillation [30]. The extraction efficiency depends on the solvent's polarity, which have to be sufficient to remove sulfur compounds. Examples of polar solvents include those with high values of the Hildebrand solubility parameter deltas as shown below in Tabel1. Liquids with a delta higher than about 22 have been successfully used to extract these compounds [5,13].

Table 1. Hildebrand solubility parameter delta for some solvents

Solvent	Hildebrand values (delta)
Acetone	19.7
Butyl Cellosolve	20.2
Carbon disulfide	20.5
Pyridine	21.7
Cellosolve	21.9
DMF	24.7
n-Propanol	24.9
Ethanol	26.2
DMSO	26.4
n-Butyl alcohol	28.7
Methanol	29.7
Propylene glycol	30.7
Ethylene glycol	34.9
Glycerol	36.2
Water	48.0

Polarity, however is not the only criteria for the selection of suitable solvents. Methanol, for example has sufficient polarity, but its density, 0.79 g/cc, is about the same as that of typical light diesel oil. Other properties such as boiling point, freezing point, and surface tension need to be considered carefully to evaluate the potential for separation and recovery of the solvent for recycling and reuse [5,13].

Zhao Dishum et al [5] in his review of desulfurization based on selective oxidation has indicated that there are two main catalysts used for selective desulfurization. These are organic acid and polyoxometalates. Organic acids include formic acid, acetic acid and so on. Polyoxometalates have long been studied for oxidation reactions, particularly, the polyoxometalate/hydrogen peroxide system for organic substrate oxidation. Little work however, has been reported on the detailed mechanistic and kinetic studies for oxidation of organic

sulfur compounds in a polyoxometalate/hydrogen peroxide system. One recent example was the oxidation of thioether by polyoxometalate/t-butyl hydrogen peroxide in a non-aqueous system [5,21]. More recently, some work reported the following trend for sulfur compound oxidation reactivity in a formic acid/H_2O_2 system [5,64]:

methylphenylsulfide> thiophenol>diphenylsulfide >4,6-dimethyldibenzothiophene > 4-methydibenzothiophene > dibenzothiophene > benzothiophene > Thiophenes.

The catalytic oxidation process includes various oxidants such as nitrogen oxides, nitric acid, hydrogen peroxide, ozone, t-BuOOH, oxygen, air, peracids, etc. The oxidation of thiophene derivatives with H_2O_2 is known to take place over various catalytic systems, such as HCOOH, CCl_3COOH, CF_3COOH, methyltrioxorhenium(VII), and phosphotungstic acid [30-38].

Yen, et al. reported in, USA 6,402,939 that organic sulfur compounds can be removed from a fossil (or petroleum-derived) fuel by a process that combines oxidative desulfurization with the use of ultrasound. The oxidative desulfurization is achieved by combining the fossil fuel with a hydroperoxide oxidizing agent in the presence of an aqueous fluid, and the ultrasound is applied to the resulting mixture to increase the reactivity of the species in the mixture [33].

Recently there has been much interest in the deep desulfurization of different fuels by photochemical reaction and liquid-liquid extraction. Some papers have been published looking at this approach where some model compounds such as DBTs were photodecomposed by UV light in the organic phase and the resulting sulfur compounds being removed in to water or acetonitrile phase [39-42].

There has also been some work conducted on a process based on the formation and subsequent precipitation of S-alkylsulfonium salts. This is accomplished by reacting sulfur–containing compounds such as DBTs and BTs with alkylating agents, CH_3I and $AgBF_4$ in the presence of dichloromethane. The products were removed as precipitates under moderate conditions. Such reactions suffer from selectivity where other aromatic hydrocarbons can also undergo methylation [43-45]

Some work has been reported on desulfurization of light oils based on the formation and subsequent adsorption of N-tosylsulfimides, produced by the reaction of the sulfur compounds in the light oils, with chloramine T (sodium N-chloro-p-toluenesulfonamide) [46]. In this work the dibenzothiophenes (DBTs) are converted by the reaction with chloramine T dissolved in methanol, to form the corresponding sulfimides. The sulfimides of alkyl-substituted DBTs, formed during the reaction, remained in the resulting light oil, such that the deep desulfurization (0.05 wt%) failed to achieve. These compounds however were removed successfully by the addition of aluminum oxide adsorbent and the sulfur concentration of the light oil was decreased to less than 0.05 wt%. The desulfurization of high-aromatic-content light oil is relatively more difficult, because the aromatic hydrocarbons are chlorinated by reaction with chloramine T, proceeding competitively with chlorination of the sulfur compounds.

Y. Shiraishi et al. have reported their work on removing sulfur and nitrogen of light oils based on the chemical oxidation using hydrogen peroxide and acetic acid. Sulfur and nitrogen compounds, when dissolved in n-tetradecane and xylene, were oxidized under moderate conditions and removed successfully. They were

successful in reducing nitrogen to < 22% of the corresponding feed values. However, sulfur content failed to be reduced to the required deep desulfurization level (0.05 wt %). This is because the alkyl-substituted sulfones, produced during the oxidation of sulfur compounds, remain in the resulting light oils, owing to their high hydrophobicity. These, however, could be removed from the light oils by subsequent extraction, using an acetonitrile/water azeotropic mixture, such that the sulfur contents of the light oils were decreased to < 0.05 wt %, while maintaining a high oil recovery yield [47]. They also reported some work on the desulfurization of light oil based on chemical oxidation of sulfur-containing compounds over Ti-containing molecular sieve catalysts. Sulfur compounds were oxidized by catalysts and H_2O_2 to the corresponding sulfoxides and sulfones and removed successfully from the oil. However, by use of this basic process, the sulfur concentration of actual light oil failed to be reduced to the required deep desulfurization level (0.05 wt %). They indicated that this maybe due to adsorption of alkyl-substituted sulfoxides and sulfones on the surface of the catalyst, thus decreasing the catalytic activity. When desulfurization was carried out in the presence of polar acetonitrile solvent, the adsorption of these compounds onto the catalyst was suppressed significantly and deep desulfurization was achieved successfully [48].

Some work has been reported on using a catalytic system consisting of metal–sulfophthalocyanines (MPcS) and monopersulfate or hydrogenperoxide as oxidants for the dibenzothiophene oxidative desulfurization. Oxidations were conducted at room temperature in acetonitrile–water mixed solvent. The dibenzothiophene oxidation involved formation of dibenzothiophene dioxide and

biphenylsultone (dibenzo-1,2-oxathiine 2,2-dioxide), followed by hydrolysis to 2(20-hydroxybiphenyl)sulfonate and finally catalytic desulfurization to 2-hydroxybiphenyl (2-phenylphenol) and sulfuric acid;. Moreover, catalytic over-oxidation of 2-hydroxybiphenyl, with ring fission and formation of various oxidation products, among them carbon dioxide, oxalic and benzoic acid, was also observed. Among the various MPcS catalysts examined (M = Fe, Co and Ru), the ruthenium derivative exhibited the best performance with persulfate and iron derivative and hydrogen peroxide; in both cases the slow step of the process was the oxidation of dibenzothiophene dioxide to biphenylsultone [49]

The physical separation by adsorption and then solvent extraction offers a lower capital and operation cost approach. However, this approach suffers from inefficiencies due to the limited polarity difference between the sulfur organic compounds and the rest of the fuel [5,21]. There is some available technology such as S Zorb sulfur removal technology which uses a proprietary sorbent that attracts sulfur-containing molecules and removes the sulfur atom from the molecule. The sulfur atom is retained on the sorbent while the hydrocarbon portion of the molecule is released back into the process stream [21].

Song et al. at Penn State University are experimenting with a new approach called selective adsorption for removing sulfur (SARS) for ultra deep removal of sulfur from liquid hydrocarbon fuels. In this process the refractory sulfur compounds are selectively adsorbed onto the surface of the solid adsorbent but leave the coexisting hydrocarbons untouched. Also, the adsorbent should be easy to regenerate for repeated use. The adsorbent used was prepared from transition metal oxides supported on alumina [50].

There is also some literature published on the use of homogenous catalysts to cleave the C-S bond in some hindered compounds. This approach, however, suffers from the practical difficulties in separating the catalysts from the products after completion of the reaction [51-54].

A literature search indicated that little work has been done using complex metals to separate the highly sulfur hindered compounds physically. Robert J. Angelici J, Iowa State University, Department of Chemistry, indicated that there are no fully characterized metal complexes that have been previously reported for removing 4,6 DMDBT. He indicated that Ru (II) in the form of $Ru(NH_3)_5(OH_2)^{2+}$ reacts with thiophene, benzothiophene, and dibenzothiophene to produce Ru complexes [55]. Angelici's approach still requires more studies to assess the removal of hindered dibenzothiophenes. Ru (II) complex undergoes oxidation in presence of air which is limiting its potential for applicability [55]. Such an approach needs to satisfy two crucial requirements to achieve successful sulfur removal. One is to make a very stable complex product of metal-organic sulfur compounds and the other one is to be able to separate this complex by some means. These requirements are very challenging which probably explains the lack of interest in this technique.

Overall, with all these developments, some work remains to be done to address the suitability of future approaches to meet the sulfur limit requirements. There are two major problems associated with ODS. First, the oxidants chosen do not always perform selectively. Some oxidants cause unwanted side reactions that reduce the quantity and quality of the light oil. The second problem is the selection of a suitable solvent for the extraction of the sulfur compounds. Using the wrong

solvent may result in removing desirable compounds from the fuel or extracting less than a desired amount of the sulfur compounds from the fuel, in either case, the consequences can be costly.

There is also no detailed work to define the appropriate conditions in terms of the optimum temperature, oxidants, catalysts, solvents/fuel ratio for extraction, and the impact of such solvents extraction on fuel quality. So the ODS approach still needs further research, especially in the area of designing the appropriate selective catalysts. Therefore the objective this study is to address such concerns and provide a detailed mechanism of the above mild oxidization-extraction method. The study will explore the possibility of developing means of forming metals-sulfur organic compounds complex for sulfur removal without using hydrogen at lower operation conditions. Such a method offers a very cost effective route if proven to be successful.

CHAPTER 2

EXPERIMENTAL WORK

Materials

2.1 Fuels

A sample of hydrotreated diesel was obtained from Rabigh Refinery, whilst an FCC gasoline sample was obtained from Jeddah refinery

2.2 Chemicals and solvents

Dibeznothiophene (DBT) (98% produced by ALDRICH with molecular formula $C_{12}H_8S$ and molecular weight 184.26). Formic acid 85% and hydrogen peroxide 30% were obtained from Riedel-de Haen. Hydrochloric acid 47%, acetic acid 98% hexane HPLC grade and toluene HPLC grade were purchased from fisher scientific. 1- Hexene 97% with was obtained from ALDRICH Chemicals. Sulfur standards were purchased from Sigma-Aldrich, Chem Sources, Antek, Chiron, and Phillips Petroleum.

2.3 Instrumentations.

The following analytical tools and techniques were used for identification and quantification purpose of sulfur components before the oxidation and further during the experiments.

Total Sulfur Determination. An Antek 9000 was used to quantify the total sulfur in diesel and model compounds. A three-point linear curve fit was applied for calibration using dibenzothiophene in HPLC grade toluene. A correlation coefficient of 0.994 was obtained. Quality check reference standards were obtained from Accua standard Corporation

Sulfur speciation. A Hewlett-Packard model HP-6890 N series gas chromatograph was used for sulfur speciation. It was equipped with a split/splitless injector, HP- G1512AX automatic sampler and HP atomic emission detector G-2350A (GC-AED). The chromatograph was fitted with a 30 m X 0.25 mm X 0.25 mm J&W column. Injector temperature was kept constant at 300^{O}C and the split ratio used was 1:100 with a sample amount of 1µl. The oven temperature was started at 50^{O}C, and raised to 250^{O}C at a rate of 10^{o}C/min. and then held for 10 min. The sulfur emission line at 181 nm was used for detection. The recipe requires both hydrogen and oxygen reagent gasses. The cavity and water temperatures were 250^{O}C. Solvent back flushing was used for model compounds and the diesel work.

A Hewlet Packard model 6890N Gas Chromatography/ Mass Spectroscopy Detector system (GC-MSD) was used for the identification of sulfur and corresponding sulfones formed during the oxidation process. The GC-MSD was set up with column DB-1, 60m, 0.25mm ID, 0.25mm film thickness. The GC temperature program used was Ti=80°C for 3 minutes. The temperature was then ramped @3°C/min to 320 °C and held for 20 minutes. The carrier gas used was Helium at 1.3ml/min. Injection temp was set at 250°C. The MS parameters were as follows: total scan from 20 to 600 mass units at a scan rate of 2.56scan/sec, Electrical energy 70eV, MS source temp 230°C.

Model compound characterization. A Differential Scanning Calorimetry (DSC 2920) instrument from TA instruments was used to study the melting behavior of the original DBT and its oxidized products, sulfones. The DSC scan was recorded

by heating approximately 5 mg of each sample from room temperature to 350°C at a rate of 10°C/min under a helium atmosphere. A Nicolet Magna 860 Fourier Transform Infrared spectrophotometer (FTIR), with beam splitters and detectors covering the range from 4,000 cm^{-1} to 400 cm^{-1}.was used for IR analysis. The samples were analyzed as a powder using the DRIFT Accessory. NMR ^{13}C NMR analysis was performed on an instrument manufactured by Varian instruments 400 MHZ at ambient temperature. Chloroform was used as the solvent. ChemWindow 6.0 Spectroscopy from Bio-Rad Laboratories, was used to predict the C^{13} chemical shift for DBT and oxidized DBT. The FEI-Philips Field-Emission XL30 Environmental Scanning Electron Microscope (ESEM-FEG) was used to determine elemental composition of compounds formed during oxidation of model compounds. The sample was submitted as is and no pretreatment was performed for the analysis. GC-Mass Spectrometry on the Micromass AutoSpec-Q (Manchester, UK) was used to determine the molecular weight. The MS was tuned at a minimum resolution of 1000 on a 10% valley. The MS source temperature was set at 200°C and the electron energy was at 70eV, while the trap current was set to 300mA. The MS was run in a magnet mode where the mass was scanned from 20- 600 amu at a scan rate of 1.5 second/decay

2.4 Preparation of the model compound and hydrogen peroxide mixture

A mixture of 0.5g of DBT, 40g of toluene and 59.5g of hexane was prepared. Hydrogen peroxide and formic acid mixtures for all experiments were freshly prepared each time. A mixture of 11g of 98% hydrogen peroxide and 21.6g of 30% formic acid was prepared. Oxidation of the model compound was carried out at

room temperature, 50 °C and 80 °C. The reaction of the DBT model was conducted initially at 50°C using formic acid and hydrogen peroxide for about 2 hours whilst stirring. Then, during the cooling process a white precipitate was formed. After washing and drying, the product was analyzed to determine the composition and structure of the product.

2.5 The temperature effect

A mixture of 200ml consisting of 0.5% DBT, 40% toluene and 59.5% hexane (all w/w) was prepared. Three 50ml samples were run separately under reflux in order to eliminate any possible evaporation. These samples were run in a sequence to be able to collect the samples and run them in a timely manner. First, the sample at room temperature was run then followed by samples at 50°C and 80°C respectively. Samples were collected at different times: 0, 10, 50, and 90 minutes and subjected to GC-MS analysis. The peak area of DBT was monitored and used as an indicator for any change. At time zero the area account of DBT was used as 100 % as baseline for all these experiments. The reduction of the DBT area was compared to zero time and plotted against time.

2.6 Acid selectivity

Three experiments using HCL, formic acid and acetic acid were conducted at 50°C. In these experiments, acids were prepared and premixed in a 1:1 mole ratio, then immediately added to 50 ml of the DBT model compound and heated at 50°C with continuous stirring. Samples were collected at different time intervals and analyzed by GC-MS. The DBT consumption was used to monitor the oxidation process.

2.7 Solvent selectivity

2.6g of a mixture of 11g of 98% hydrogen peroxide, and 21.6g of 30% formic acid were added to two samples of 100ml of hydrotreated diesel. The two samples were heated at 50°C for 90 minutes. Then both samples were extracted with 15ml of distilled water. The upper layer was submitted for total sulfur determination. Then, the top layer of each sample was separated. One sample was washed again with acetonitrile and one with methanol and the diesel layer of both samples were submitted to total sulfur determination.

2.8 Olefin effect

Two samples of the model compound, one including hexane and the other including 1-hexene, were used at the same weight percent of 59.5%. 2.6g of a mixture of hydrogen peroxide and formic acid were added to both samples and heated at 50^{o}C. Samples were collected at different times: 0, 10, 50, and 90 minutes and subjected to GC-MS analysis. The percent ratio of the oxidized DBT over the non-reacted DBT was monitored at different times at a temperature of 50^{o}C

2.9 The effect of metal salts on the oxidation of DBT

One gram of each metal salt, ferric chloride, cadmium (II) chloride, cobalt (II) acetate and copper metal was added to 50ml of DBT model compound. All experiments were heated at 50°C and samples were collected at 0,5,15,30,50,90 minutes and submitted to GC-MS analysis.

2.10 Hydrogen peroxide/formic acid mixture concentration effect

Six experiments were carried out to study the effect of H_2O_2/formic acid mixture concentrations on sulfone formation. Concentrations used were 0, 1.3%,

2.6%, 3.9%, 5.2% and 6.5% and mixed with 50ml of hydrotreated diesel containing 1022ppm of sulfur. All the samples were heated at 50°C for 90 minutes. Then, the samples were cooled down and washed with 50ml of distilled water to remove any remaining acid/H_2O_2 mixture. The samples again washed with 10ml of acetonitrile and mixed well and left for 30 minutes to settle down. The diesel layer of each sample was separated and washed again with another 10ml acetonitrile. The acetonitrile layers were discarded and the diesel samples were washed one more time with 10ml of acetonitrile and the diesel layers samples were submitted for total sulfur determination. Three more experiments were run at 100°C using 1.3%, 3.9%, 6,5% acid/H_2O_2 mixtures for 90 minutes.

2.11 Sulfones speciation in diesel

Hydrotreated Gas Oil (Diesel) (100ml) was treated with 2.6g of a mixture containing 21g of 95% formic acid and 11g of 30% hydrogen peroxide. The mixture was stirred and heated at 50ºC for 120 minutes. The aqueous acid phase was separated in a 150ml separatory funnel and discarded. The oil phase was extracted with 100ml of acetonitrile. The acetonitrile extract was washed twice with 50ml of reagent grade hexane, and the washings discarded. The washed 100ml extract was evaporated overnight in a stream of nitrogen.

2.12 The effect of acetonitrile on diesel quality

10, 20 and 50ml of acetonitrile were added to three 50ml samples of hydrotreated diesel separately. All were mixed well and left at room temperature for settling down for one hour. The samples were separated and the volume of each layer was determined. The same experiments were repeated and left for settling down overnight and the volume for each layer was measured again.

CHAPTER 3

RESULTS AND DISCUSSIONS

The world-wide trend for cleaner fuel has imposed increasingly severe specifications on transportation fuel. Meeting future requirements of less than 50ppm sulfur requires a deep desulfurization process. Therefore, sulfur speciation becames a necessary stage in order to provide good knowledge of the sulfur types and to gain an understanding of their chemical and physical behavior during the desulfurization process. Generally, gas chromatography equipped with selective sulfur detectors and gas chromatography/mass spectrometry are used to identify the sulfur compounds in hydrocarbon fuels. Previous studies have described methods for sulfur speciation in petroleum products [56-62]. The American Society established a standard method for Testing and Materials (ASTM D-5623) that covers the determination of volatile sulfur-containing compounds in light petroleum.

3.1 Sulfur Speciation of FCC Gasoline

The major finished gasoline component in some European countries and in North America comes from Fluid Catalytic Cracked (FCC) gasoline. It is documented that FCC gasoline contributes about 98% of the sulfur that is contained in today's finished gasoline. The octane of full boiling range (C5 – 200 °C) FCC gasoline comes from the olefins in the light FCC portion (C5 – 70 °C) and the aromatics in the heavy FCC portion (70 – 200 °C). Fortunately, for the light FCC gasoline, the sulfur can be removed by caustic treating process, which does

not affect the olefins in anyway. The heavy FCC gasoline extraction can affect the olefin content and consequently reducing the octane of the finished product. Therefore, the need to identify the sulfur in gasoline becomes essential to design the appropriate approach to deep desulfurization [63-66].

Sulfur speciation of FCC Gasoline has been completed using GC-AED and GC-MS, and by analyzing reference materials and standards including mercaptans, sulfides, thiophene, 2-methyl and 3-methyl thiophenes, benzothiophene, and methyl benzothiophenes.

As mentioned above some work has been done to identify the sulfur compounds in gasoline. The purpose of this step is to look at the certain gasoline that is produced from specific process to design the experimental approach for the deep desulfurization. Table 2 below includes some properties of FCC gasoline. The chromatograph in figure 4 and table 3 demonstrate the sulfur compounds that have been identified in the FCC gasoline.

Table 2. Some Chemical and physical properties of typical FCC gasoline.

Test Description	Test method	FCC Gasoline
Total Acidity (mg KOH/g)	D3242orD974	0.051
Aromatics (FIA) (V %)	D-5134 M	16.9
Olefins (FIA) (V %)	D-5134 M	38.4
Mercaptan Sulfur (W %)	D-3227	0.0009
Total Sulfur (W%)	D-5453	0.1045
Distillation, °C IBP	D-2887	31.1
10% Recovery	D-2887	52.1
50% Recovery	D-2887	112.0
90% Recovery	D-2887	178.9
End Point	D-2887	218.2
Residue, V %	D-2887	1.5
Loss, V %	D-2887	2.0
Gravity API @ 60° F	D-4052	58.9
Vapor Pressure (kPa)	D-5191	9.0
Water by Karl Fisher PPM	D-1744	122
Octane Rating Research	D-2699	95.2

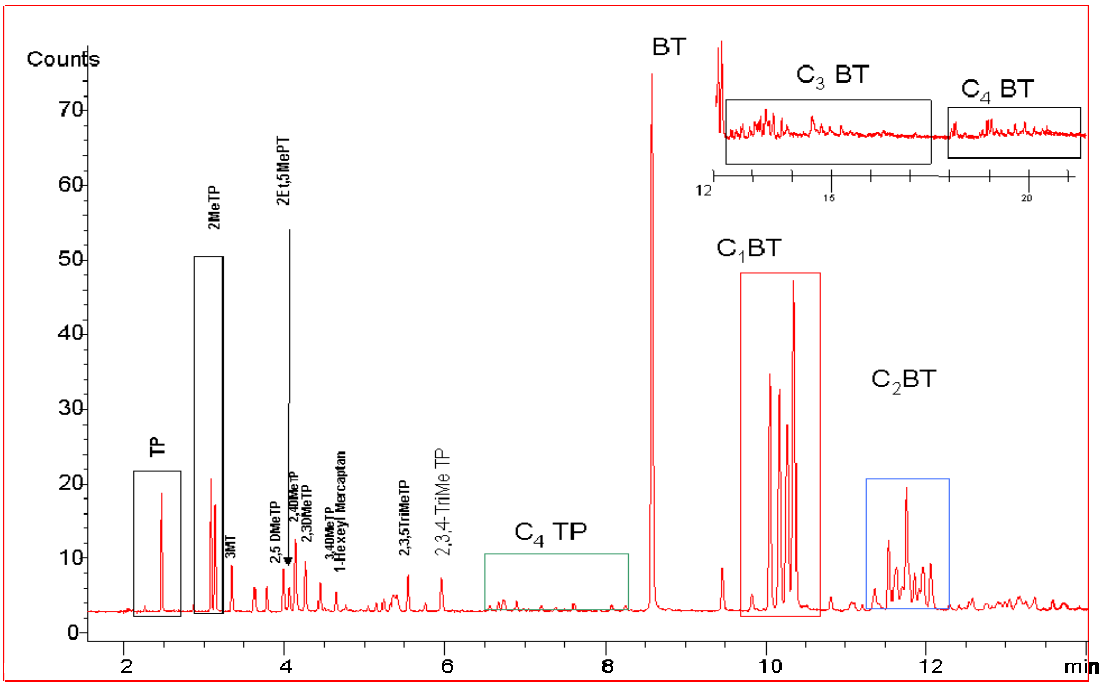


Figure 4. Sulfur speciation in FCC gasoline

Table 3. Retention Times for Sulfur Species in FCC Gasoline

RT	Compound	RT	Compound
1.95	Isobutyl Mercaptan	7.40	C4 Thiophenes
2.50	Thiophene & T-Butyl Mercaptan	7.65	
3.10	2-Methyl Thiophene	8.00	
3.20	3-Methyl Thiophene	8.15	
3.70	2-Ethyl Thiophene	8.30	
4.00	2,5-Dimethyl Thiophene	8.55	Benzothiophene
4.10	2-Ethyl 5-Methyl Thiophene	10.10	7-MethylBenzothiophene
4.20	2,4-Dimethyl Thiophene	10.25	2-MethylBenzothiophene
4.30	2,3-Dimethyl Thiophene	10.30	5 & 6 Methyl Benzothiophenes
4.50	3,4-Dimethyl Thiophene	10.35	3 & 4 Methyl Benzothiophenes
4.70	1-Hexyl Mercaptan	11.25	7-Ethyl Benzothiophene
5.20	2-Ethyl-5-Methyl Thiophene	11.40	2,7 Dimethyl-Benzothiophene
5.30	3-Ethyl 5-Methyl Thiophene	11.50	2-Ethyl Benzothiophene
5.38	2-Ethyl 3-Methyl Thiophene	11.60	2,8 & 2,5 DimethylBenzothiophene
5.40	2-Ethyl 4-Methyl Thiophene	11.70	2,4-Dimethyl Benzothiophene
5.42	3-Ethyl 2-Methyl Thiophene	11.75	3,5 & 3,6-Dimethyl Benzothiophene
5.60	2,3,5 Trimethyl Thiophene	11.80	2,3-Dimethyl Benzothiophene
5.80	3-Ethyl 2-Methyl Thiophene	11.85	6,7-Dimethyl-Benzothiophene
6.00	2,3,4-Trimethyl Thiophene	11.90	5,6-Dimethyl Benzothiophene
6.60		11.95	4,5-Dimethyl Benzothiophene
6.70		12.10	3,4-Dimethyl Benzothiophene
6.80		12.35	3,5-Dimethyl Benzothiophene
6.95	C4 Thiophenes	12.50	C-3 Benzothiophenes
7.05		18.00	
7.10		18.00	C-4 Benzothiophenes
7.25		21.00	

3.2 Sulfur speciation in hydrotreated diesel.

Hydrotreated diesel was used specifically to eliminate most of the easy sulfur compounds that are usually removed by the conventional hydrodesulfurization process. Table 4 shows some properties of diesel used in this study. The higher the boiling range of the hydrocarbon products, the more complex sulfur identification becomes. Previous work on sulfur identification of some commercial diesel fuel [30] has identified the existence of both alkyl benzothiophenes and alkyl dibenzothiophenes. The graph in figure 5 indicates existing derivatives, the majority of them being alkyl dibenzothiophenes. Some of these isomers are co-eluted and it became very difficult to separate them for identification. Another problem is that the diesel includes high concentrations of aromatic hydrocarbons in relation to their sulfur concentrations. This represented a challenge to devise a method that could separate the sulfur aromatics from the remaining hydrocarbon aromatics. However, there has been some work on the sulfur speciation in diesel where some of the sulfur compounds have been identified [48,59-60].

To illustrate the complexity of existing types of ring distributions of hydrocarbons, including sulfur aromatic rings, Supercritical Fluid Chromatography (SFC) was used. The method is based on the procedure given by the ASTM D-5186. Table 5 demonstrates the ring number distributions of typical diesel of Arabian light crude oil. The graph in Figure 6 shows the ring distributions of light, medium and heavy diesel fractions of Arabian light crude.

The identification was based on literature references motioned earlier listing the exact identification of individual isomers of alkylated thiophenes,

benzothiophenes, naphthothiophenes, and dibenzothiophenes, in Naphtha and Mid-Distillate, and through the use of standards obtained from Sigma-Aldrich, Chem Sources, Antek, Chiron, and Phillips Petroleum.

The results of identification and measurement of 58 sulfur-containing components appear in Table 6, which gives retention order and retention time, molecular structure, molecular weight, sulfur weight (%). It is worth highlighting that all these sulfur compounds that have been identified in the hydrotreated diesel include mainly refractory sulfur compounds. Typical non-hydrotreated diesel has more sulfur compounds that include mercaptans, sulfides and disulfides.

Table 4. Some properties of hydrotreated diesel.

Test Description	Test method	Hydrotreated Diesel
Color	D-1500	0.5
Total Sulfur (W%)	D-5453	0.1045
Distillation, °C IBP	D-2887	216
10% Recovery	D-2887	253
50% Recovery	D-2887	314.0
90% Recovery	D-2887	391
End Point	D-2887	401
Specific Gravity @ 60° F	D-4052	0.8530
Pour Point	D-97	12
Cloud Point	D-2500	15
Flash point °C	D-93	67
Copper Corrosion	D-130	1a

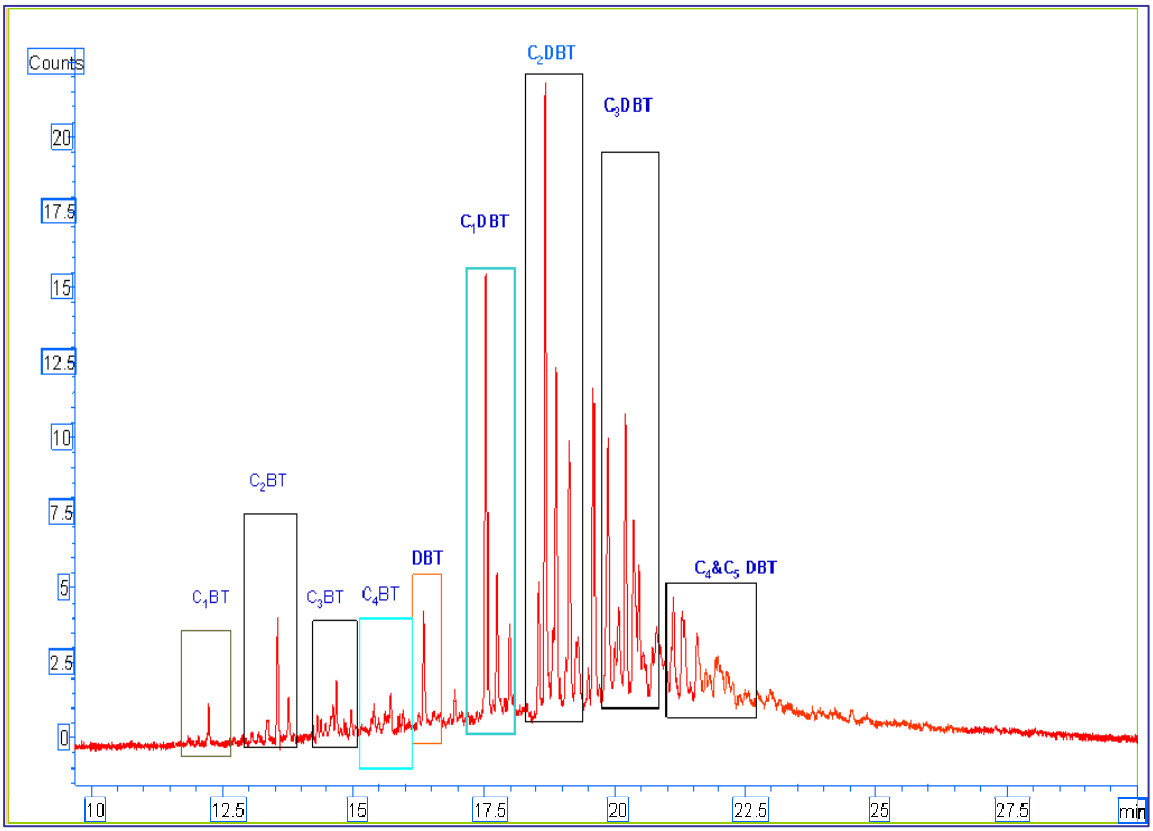


Figure 5. Sulfur compounds in hydrotreated diesel.

Table 5. Ring Number Distribution in 490-725 ºF Diesel

Retention Time minutes	Ring Number	Relative Area %	Aromatics Volume %
4.22	One Ring	33.79	7.51
5.54	Two Ring	41.59	9.24
7.5	Three Ring	18.42	4.09
9.43	Four Ring	6.19	1.38
Sum of Ring Peaks			22.22

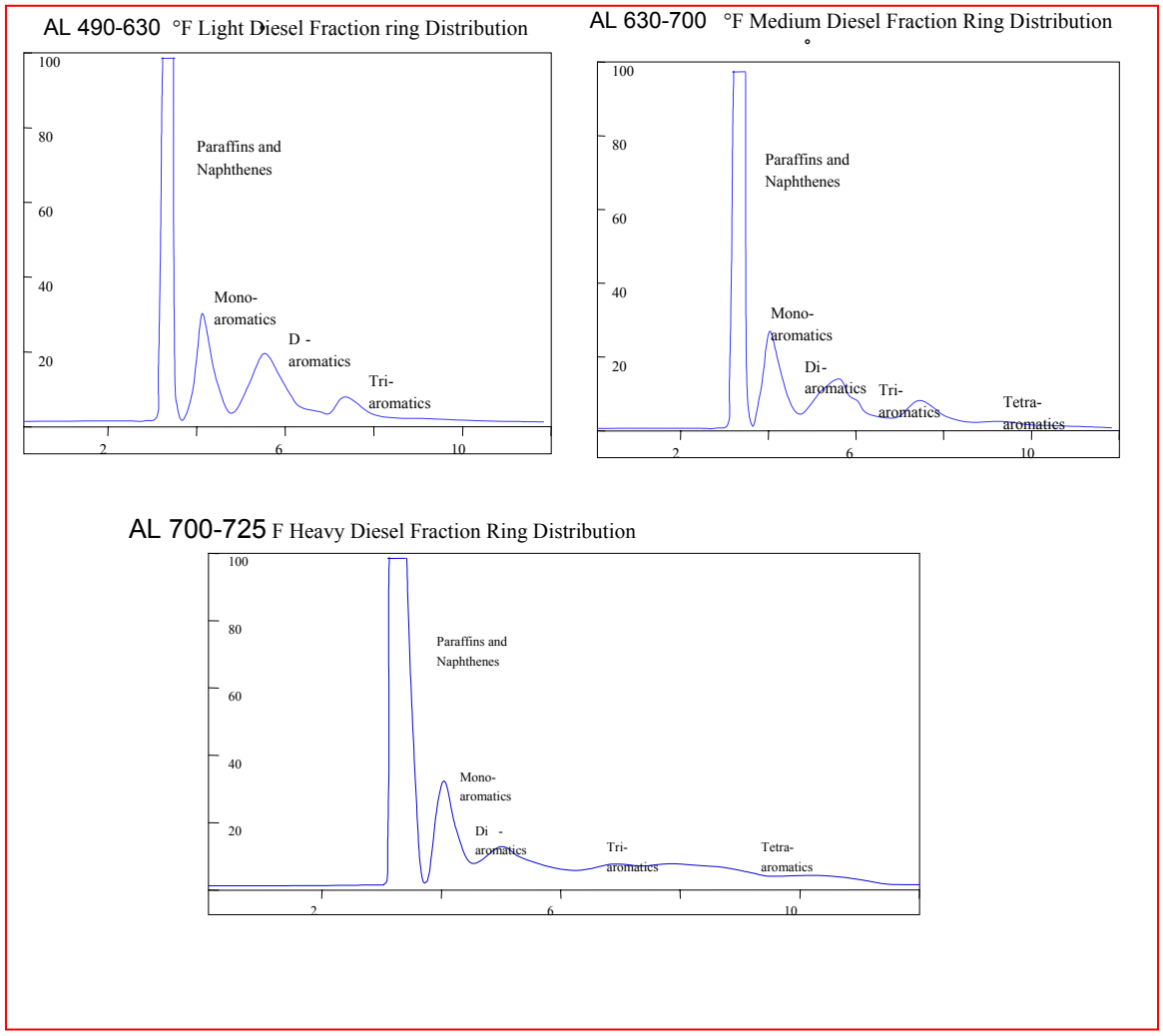


Figure 6. Ring distributions of different diesel fractions

Table 6. Sulfur species in typically hydrotreated diesel.

Number	R. Time	Component	MW	% Sulfur
1	9.08	2,5-Dimethyl Benzothiophene	162	19.75
2	9.28	2,7-Dimethyl Benzothiophene	162	19.75
3	9.38	3,4-Dimethyl Benzothiophene	162	19.75
4	9.56	2-Ethyl Benzothiophene	162	19.75
5	10.12	2,4,5-Trimethyl Benzothiophene	176	18.18
6	10.31	2,4,7-Trimethyl Benzothiophene	176	18.18
7	10.41	2,4,6-Trimethyl Benzothiophene	176	18.18
8	10.57	2,5,7-Trimethyl Benzothiophene	176	18.18
9	10.76	3,4,7-Trimethyl Benzothiophene	176	18.18
10	10.96	2-Methyl 4-Ethyl Benzothiophene	176	18.18
11	11.08	4-Methyl-2-Ethyl-Benzothiophene	176	18.18
12	11.25	2,3,4,7-Tetramethyl Benzothiophene	190	16.84
13	11.36	2,4,5,7-Tetramethyl Benzothiophene	190	16.84
14	11.45	2,3,6,7-Tetramethyl Benzothiophene	190	16.84
15	11.53	2,3,4,6-Tetramethyl Benzothiophene	190	16.84
16	11.68	2,7-Dimethyl 4-Ethyl Benzothiophene	190	16.84
17	11.79	3,6-Dimethyl 4-Ethyl Benzothiophene	190	16.84
18	11.94	4,7-Dimethyl 2-Ethyl Benzothiophene	190	16.84
19	12.05	2,5-Dimethyl 1-Ethyl Benzothiophene	190	16.84
20	12.11	2,7-Diethyl Benzothiophene	190	16.84
21	12.23	2,4-Diethyl Benzothiophene	190	16.84
22	12.30	2-Ethyl 3,4,5-Trimethyl Benzothiophene	204	15.69
23	12.46	7-Ethyl 2,4,5-Trimethyl Benzothiophene	204	15.69
24	12.66	4-Ethyl 2,3,5-Trimethyl Benzothiophene	204	15.69
25	13.20	7-Ethyl 2,3,5-Trimethyl Benzothiophene	204	15.69
26	13.38	4-Methyl-2,5-Diethyl Benzothiophene	204	15.69
27	13.45	4-Methyl-3,5-Diethyl Benzothiophene	204	15.69
28	13.59	2,4,5-Triethyl-Benzothiophene	218	14.68
29	13.83	Dibenzothiophene	184	17.39
30	13.97	2,3,6-Triethyl-Benzothiophene	218	14.68
31	14.06	3,5,6-Triethyl-Benzothiophene	218	14.68
32	14.25	2,4-Diethyl-2,6-Dimethyl Benzothiophene	218	14.68
33	14.36	3,5-Diethyl-2,4-Dimethyl-Benzothiophene	218	14.68
34	14.39	2,5-Diethyl-4,7-Dimethyl-Benzothiophene	218	14.68
35	14.42	2,5-Diethyl-4,6-Dimethyl-Benzothiophene	218	14.68
36	14.46	2,3,5,6-Tetramethyl-7-Ethyl-Benzothiophene	218	14.68

37	14.53	4-Methyl Dibenzothiophene	198	16.16
38	14.73	3-Methyl Dibenzothiophene	198	16.16
39	14.95	1-Methyl Dibenzothiophene	198	16.16
40	15.05	2-Methyl Dibenzothiophene	198	16.16
41	15.22	2,7-Dimethyl Dibenzothiophene	212	15.09
42	15.57	4,6-Dimethyl Dibenzothiophene	212	15.09
43	15.76	2,4-Dimethyl Dibenzothiophene	212	15.09
44	15.95	4,9-Dimethyl [2,3-b]-Napthothiophene	212	15.09
45	16.01	2,8-Dimethyl Dibenzothiophene	212	15.09
46	16.15	1,6-Dimethyl Dibenzothiophene	212	15.09
47	16.32	3,4,7-Trimethyl Dibenzothiophene	226	14.16
48	16.43	3,4,6-Trimethyl Dibenzothiophene	226	14.16
49	16.70	1,4,6-Trimethyl Dibenzothiophene	226	14.16
50	16.88	2,4,7-Trimethyl Dibenzothiophene	226	14.16
51	17.18	1,4-Dimethyl 9-Ethyl-Dibenzothiophene	226	14.16
52	17.31	2,4-Dimethyl 7-Ethyl-Dibenzothiophene	226	14.16
53	17.48	4,6-Diethyl-Dibenzothiophene	226	14.16
54	17.53	Benzo-[5,6-b]-Napthothiophene	226	14.16
55	17.60	2,4,8,9-Tetramethyl-Dibezothiophene	226	14.16
56	17.72	1,4,6,9-Tetramethyl-Dibezothiophene	234	13.68
57	18.00	1,4,7-Trimethyl-8-Ethyl Dibenzothiophene	240	13.33
58	18.13	3-Methyl-4,8-Diethyl Dibenzothiophene	240	13.33

3.3 THE OXIDATION OF MODEL COMPOUND

In order to understand the oxidation/extraction process, a model compound was prepared simulating the overall compositions of gasoline and diesel fuel. The reaction of the DBT model conducted at 50°C using formic acid and hydrogen peroxide resulted in a white participate. Melting points of both starting material DBT and the resulting oxidative product were determined. The DSC graph at figure 7 shows a comparison of the two melting points, one is typical of DBT which is about 98ºC and the other one is 234ºC. FTIR also was used for both samples (figure 8). The spectrum shows two peaks at 1280 and 1160 cm^{-1} which are characteristic of sulfone compounds. Figure 9 shows the ESEM elemental analysis of DBT before and after treatment. It clearly indicates that some oxygen has been introduced after the oxidation process. ^{13}C NMR chemical shifts before and after the oxidation treatment show slight different between oxidized DBT and the starting material. The observed change was in quarterly carbon atoms of the oxidized DBT which are 131.59 and 137.68 comparing to DBT which are 139.35 and 135.47. This upfield shift of the quarterly carbon which is close to the sulfur atom indicating an effect of some strong withdrawing group that makes this carbon atom more deshielded (figures 10 and 11). This also was noticed in carbon number 2, 4 as a result of some resonance effect. Chemical shifts were predicted for DBT and its oxidized product using ChemWindow® Spectroscopy and compared to the experimentally determined values (figure 11). The predicted and observed values are shown in figure 10. The high resolution GC-MS spectra of DBT and oxidized DBT are shown in figures 12 and 13 respectively. The molecular

mass of DBT was determined to be 184.03 which is close to the calculated value of 184.26. The oxidized product was found to have a mass of 216.03 giving a difference mass of 32 units. This additional 32-unit mass corresponds to the mass of two oxygen atoms. The GC-MS spectrum was confirmed by the library database that includes the spectrum of the DBT-sulfone (figure 14).

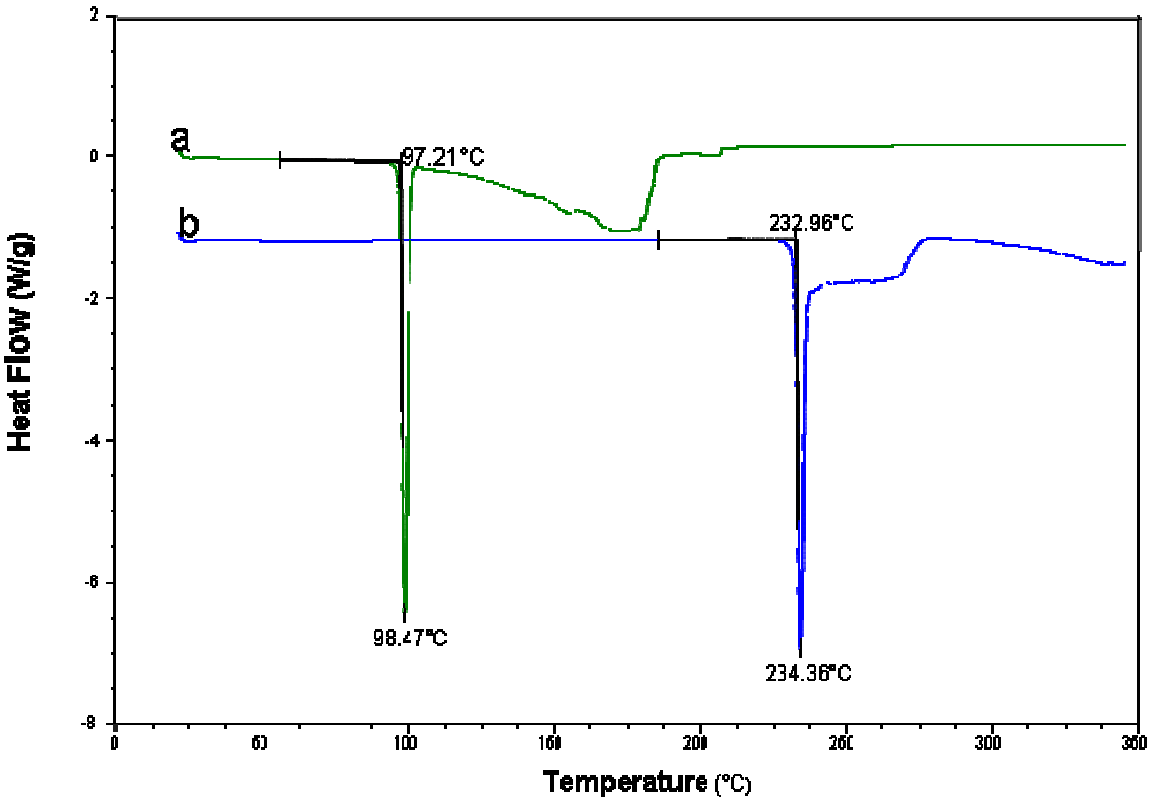


Figure 7. DSC for DBT (a) before oxidation (b) after oxidation

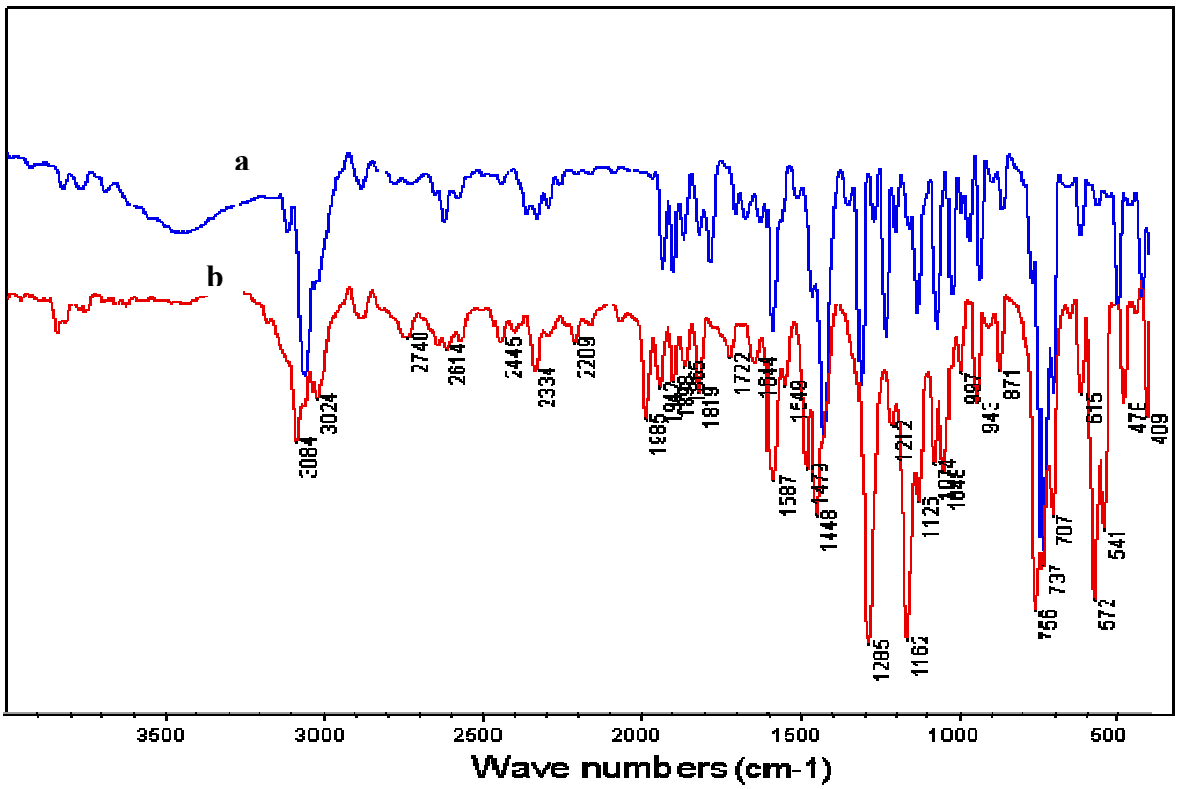


Figure 8. FTIR for (a) DBT before oxidation (b) DBT after oxidation

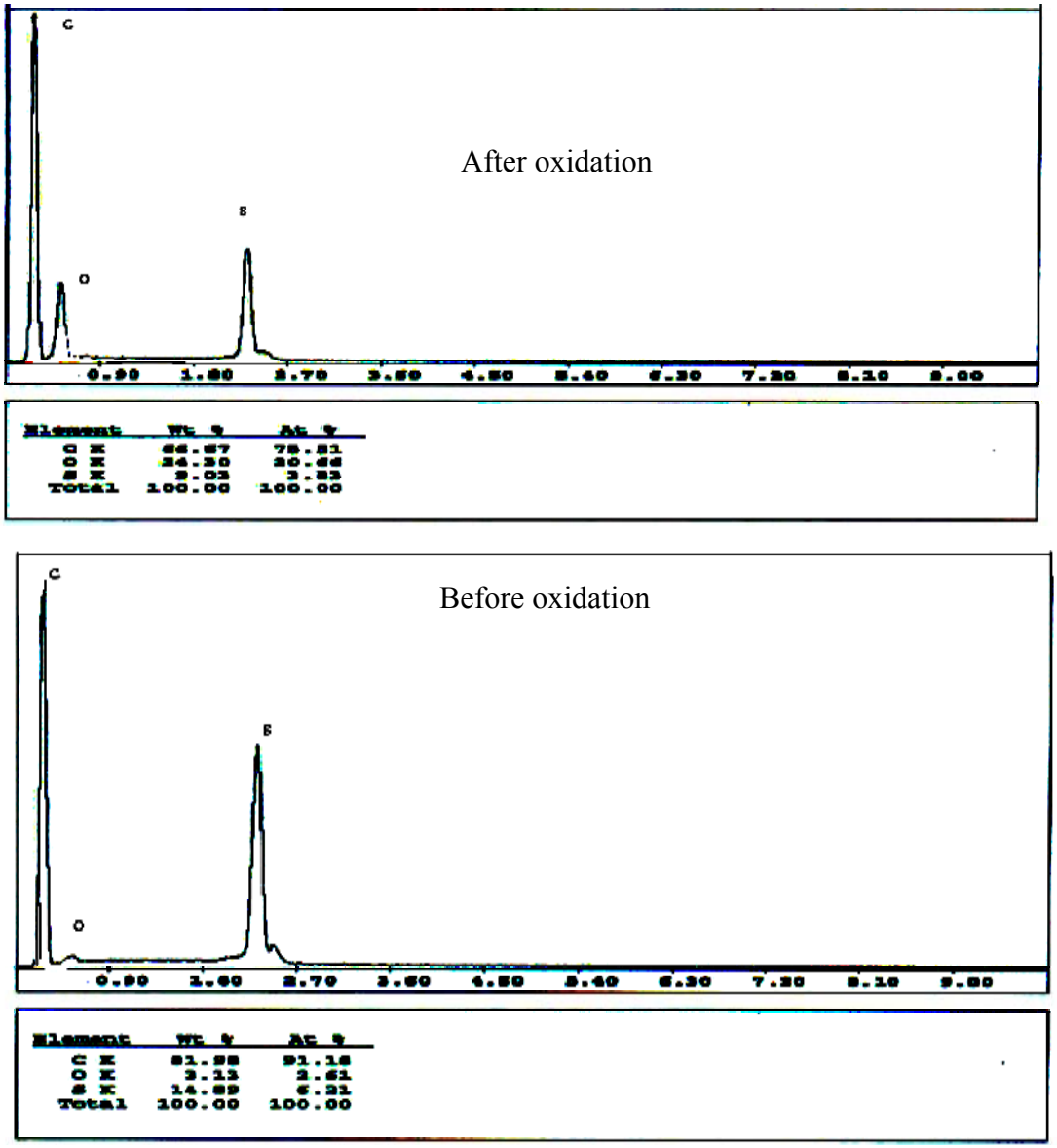


Figure 9. ESEM elemental analyses of DBT before and after oxidation

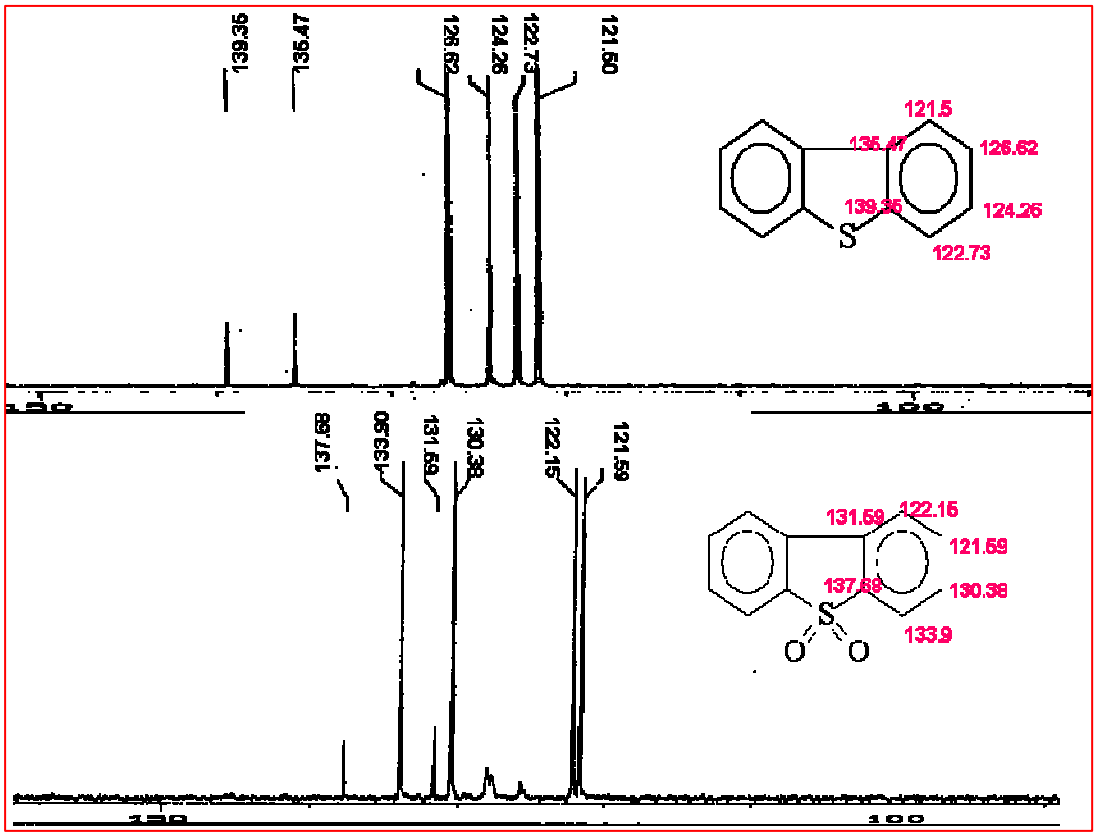


Figure 10. ^{13}C NMR for DBT and oxidized DBT

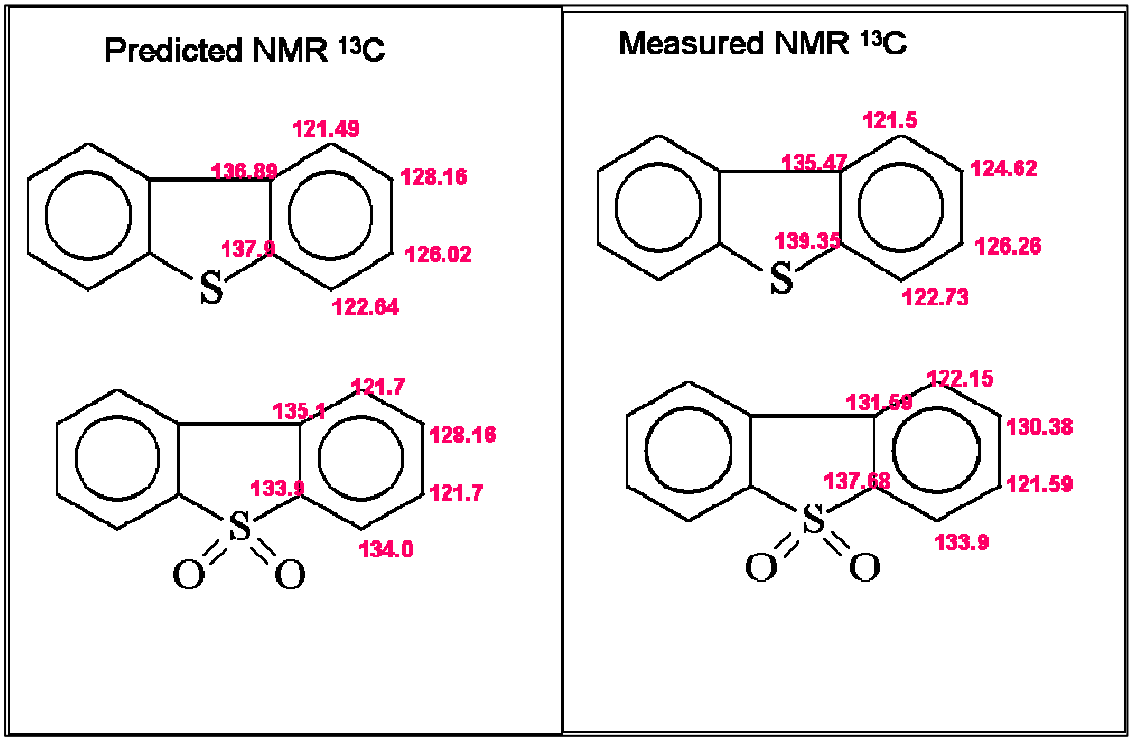


Figure 11. ChemWindow Predicted and measured chemical shifts for both DBT and its corresponding sulfone

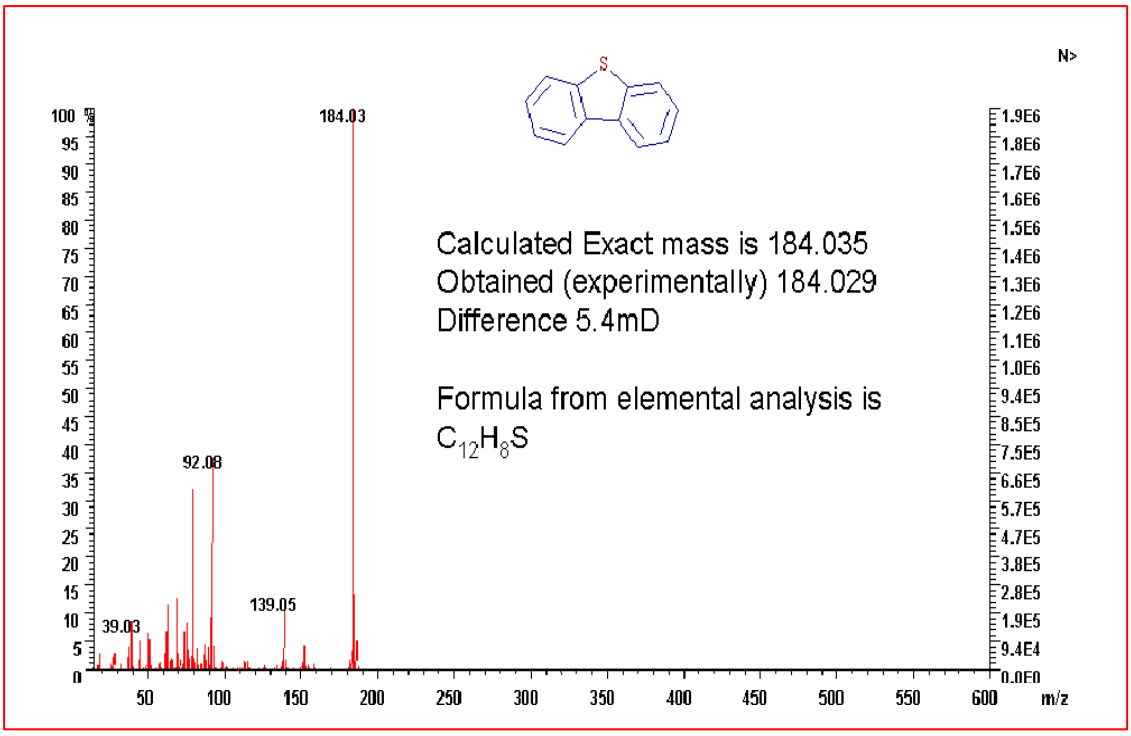


Figure 12. GC-MS for DBT

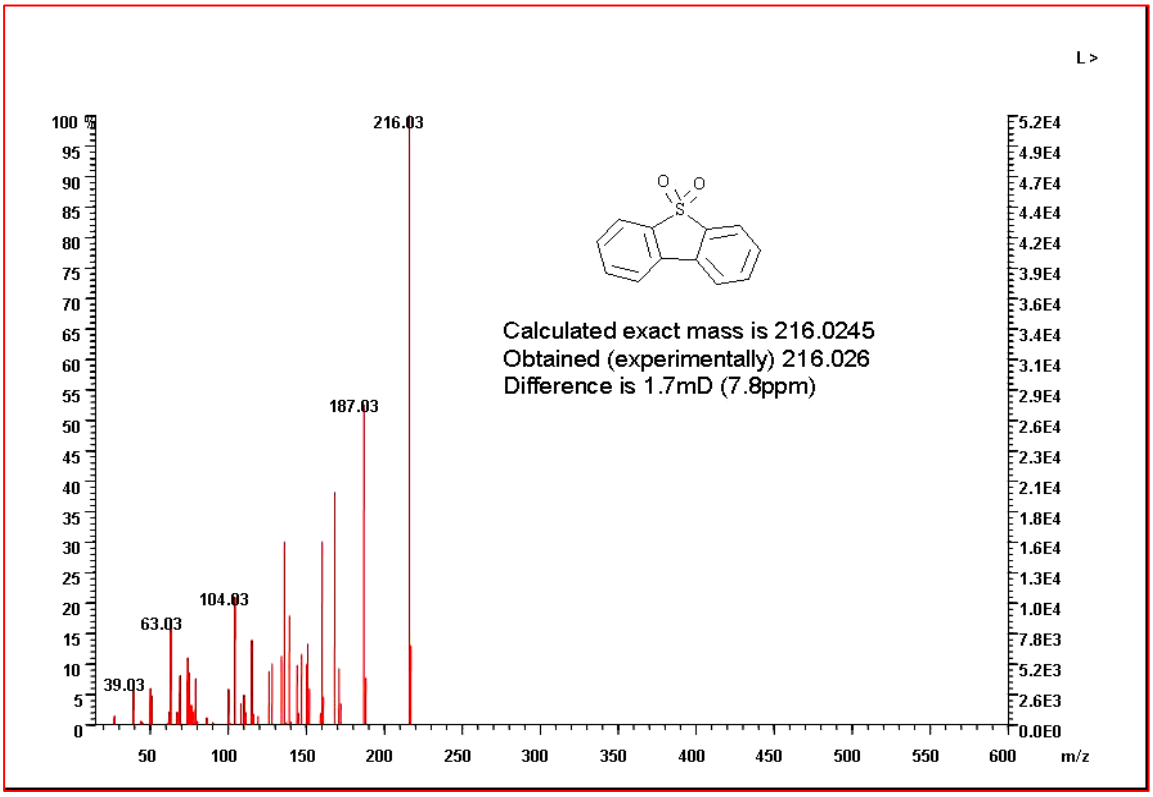


Figure 13. GC-MS for oxidized DBT

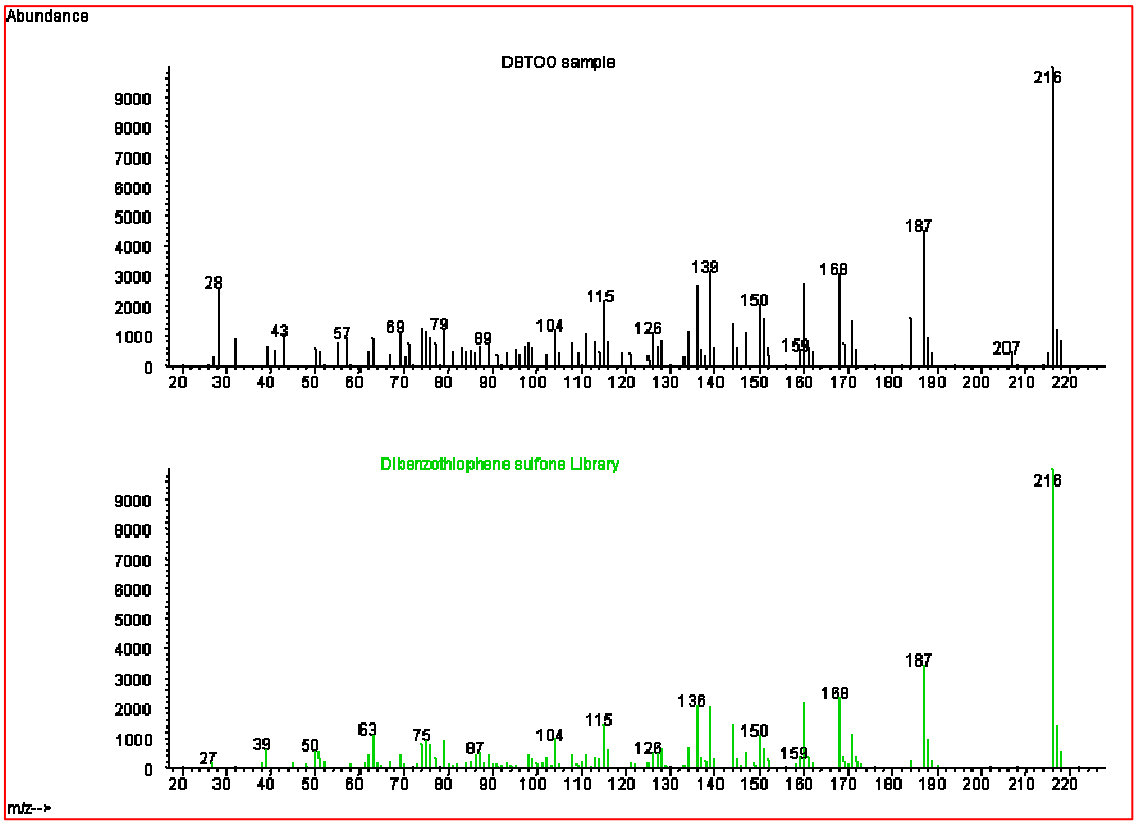
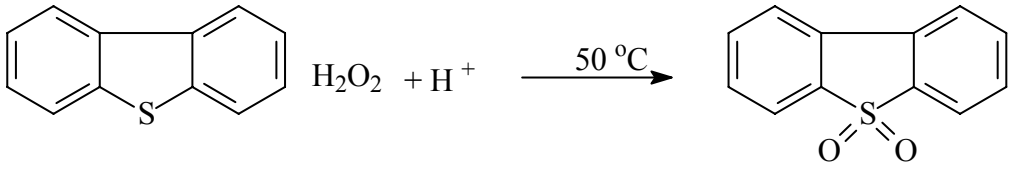


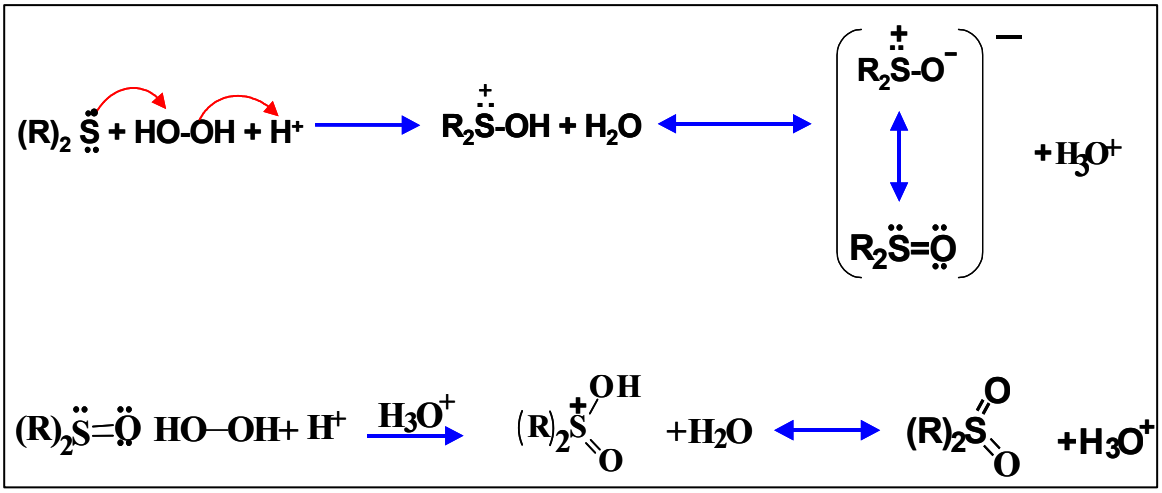
Figure 14. GC- MS spectra of DBT sulfone formed and library DBT sulfone

The above analytical results indicate that the following compound was formed during the oxidation process. This identification of the products has helped in sulfone speciation and will be discussed later.



This work will help study the oxidation of different DBT derivatives that exist in diesel fuel. It gives an indication that all hindered sulfur compounds can be oxidized and converted to their corresponding sulfones. Reviewing the reaction of

organic sulfur compounds indicated that organic sulfides could undergo the oxidation process to give either sulfoxides or sulfones [67]. The proposed



mechanism of this reaction is described below

The above-proposed mechanism has helped in gaining a better understanding of the reaction requirements for the oxidation of hindered compounds that exist in the fuels such as diesel and gasoline. It also indicates clearly that the type of catalyst, in this case formic acid, plays an important role in the oxidation process. Therefore, the oxidation of DBT at different conditions was investigated and this is described in the following sections:

3.3.1 TEMPERATURE EFFECT

The graph shown in figure 15 demonstrates the temperature effect on dibenzothiophene oxidation. At room temperature the remaining non-reacted DBT was about 70% after 90 minutes, whereas only about 20% and 6% remained at 50°C and 80°C, respectively over the same period. No abnormal behavior such as decomposition or coke formation was indicated by gas chromatography results.

Caution must be exercised at temperatures higher than 80°C which may lead to the oxidation of useful components of the fuel. It was documented that the selectivity of decomposition of hydrogen peroxide to oxygen increased with the reaction temperature [68]. It was also reported that the naphthalene can undergo oxidation to form naphthalene-1,4 dione at higher temperatures [30].

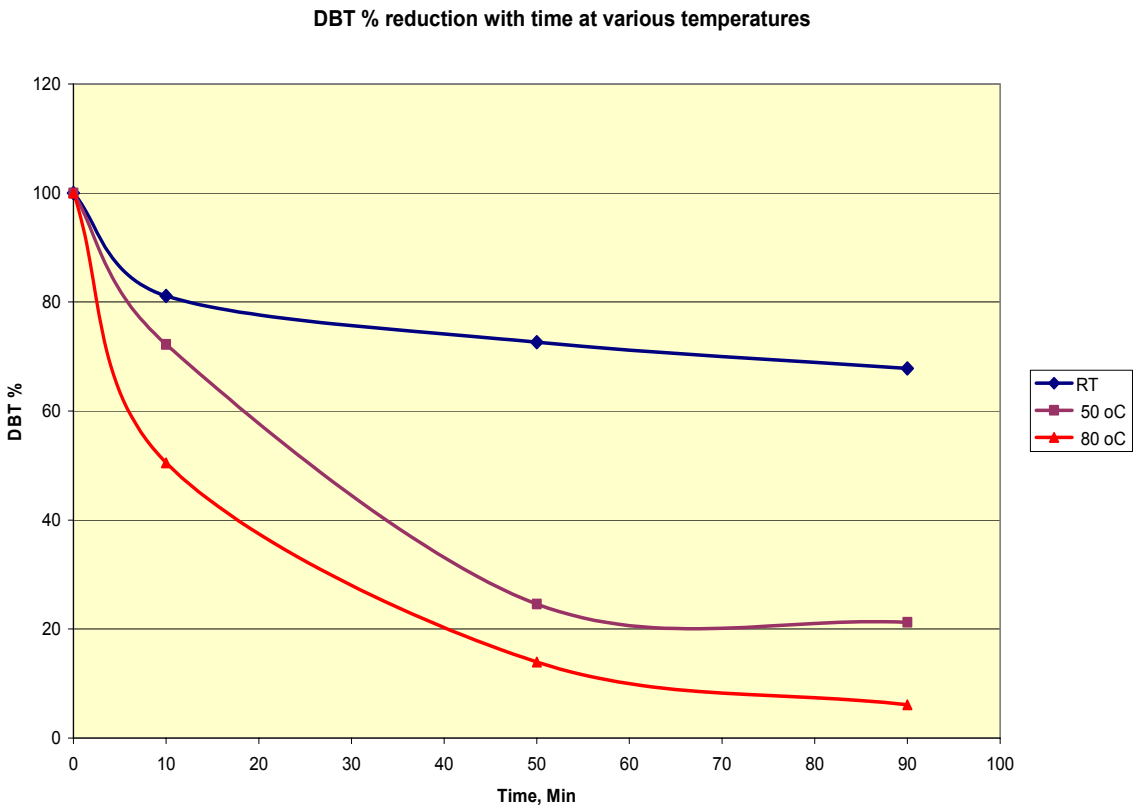


Figure 15. Oxidation of DBT at different temperatures.

3.3.2 ACID SELECTIVITY

Continuous bubbling was noticed when hydrolcloric acid and acetic acid were used. In the case of HCl, the bubbling was more vigorous and did not last long whereas in the case of acetic acid it persisted over a longer period of time. The results as showed in figure 16&17 indicate that the formic acid has a greater oxidating effect than in the case of both acetic acid and HCl. There is some oxidation in presence of HCl however; it is insignificant compared to the formic acid sample. This clearly indicates that a strong acid may accelerate the decomposition of H_2O_2 to oxygen and water resulting in a poor yield of oxidized DBT. Therefore, the result after 15 minutes in HCL sample was not included in graph 17 due to the difficulty of producing good results that could be compared to the rest of the samples. In the case of acetic acid, the reaction rate is very slow and requires a longer period of time to produce satisfactory results. The acetic acid is a relatively week acid compared to formic acid (the dissociation constant of acetic acid is $1.74\ X10^{-5}$ and formic acid is $1.78\ X10^{-4}$ at room temperature). Therefore, the reaction probably requires longer time for oxidation to occur, however during this time, the H_2O_2 can undergo decomposition which is a well known phenomenon, even at lower temperatures. This requires addition of further quantities of H_2O_2 to produce a satisfactory result.

It has been documented that acetic acid has been used successfully to oxidize sulfur compounds to sulfones [5,21,48]. In view of this, the effect of acetic acid was re-examined with a different approach. In this experiment a premixed amount of hydrogen peroxide and 50ml of DBT model compound using the same quantities and conditions as the previous experiment were prepared. During the

heating, acetic acid was added drop-wise over a ten minute period. The samples again were collected at the same time interval and after 20 hours to see the effect of a longer time. The results as shown in figure 15 confirmed earlier findings that the oxidation of DBT to its corresponding sulfone is a very slow process in the presence of acetic acid. For example the remaining percentage of non-reacted DBT after 90, and 1200 minutes was around 90% and 77% respectively. For comparison purposes, the non-reacted DBT fraction in the formic acid experiment after 50 and 90 minutes were observed to be 25% and 21% respectively.

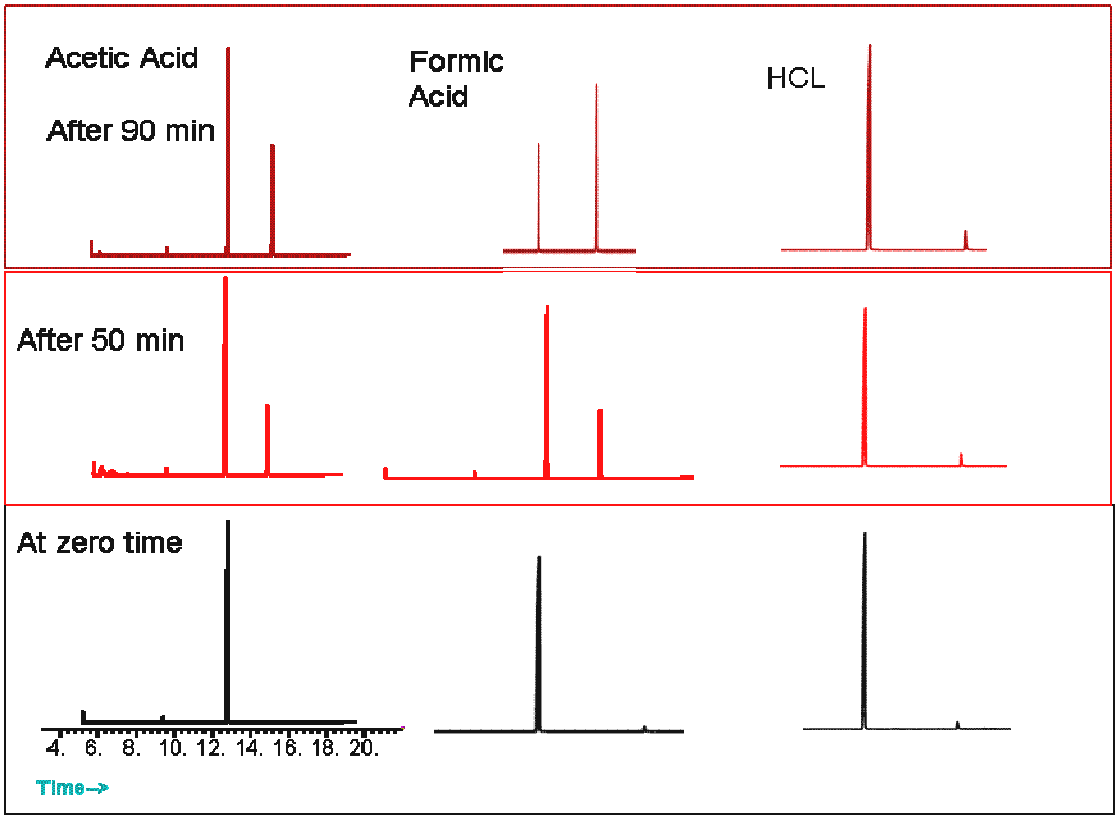


Figure 16. GC-MS Spectra of DBT and oxidized DBT by different acids

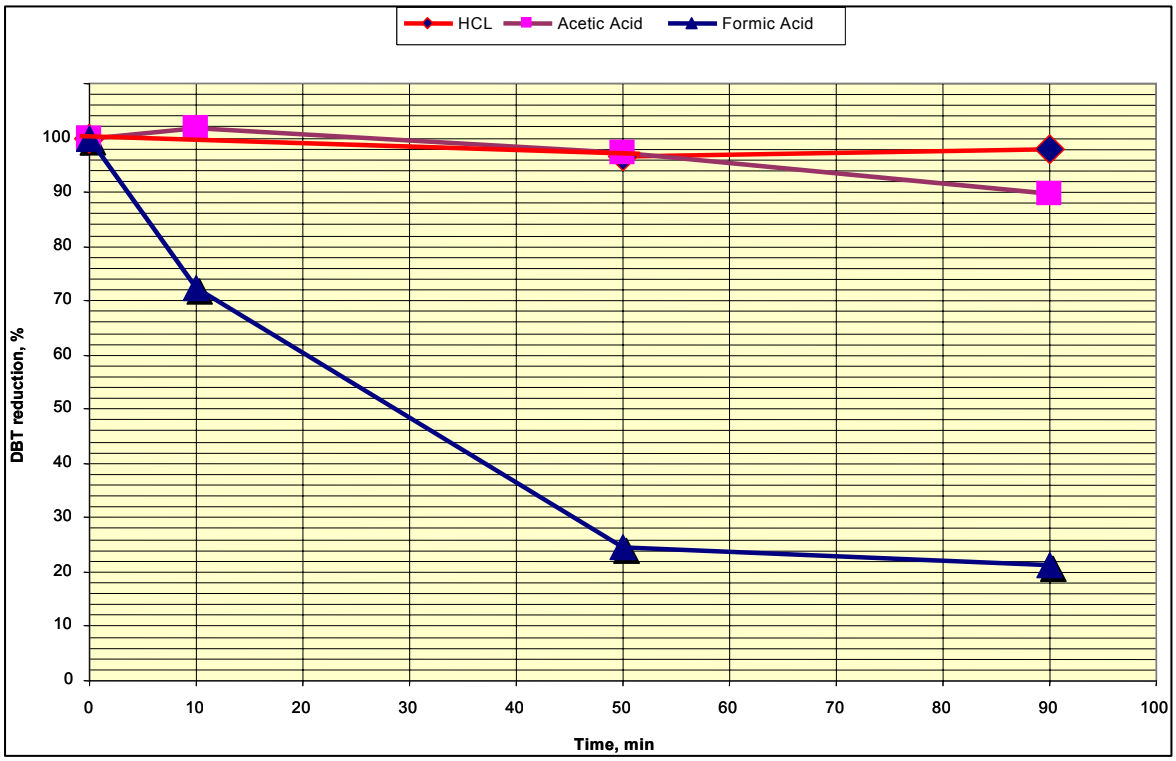


Figure 17. Oxidation of DBT in different acids.

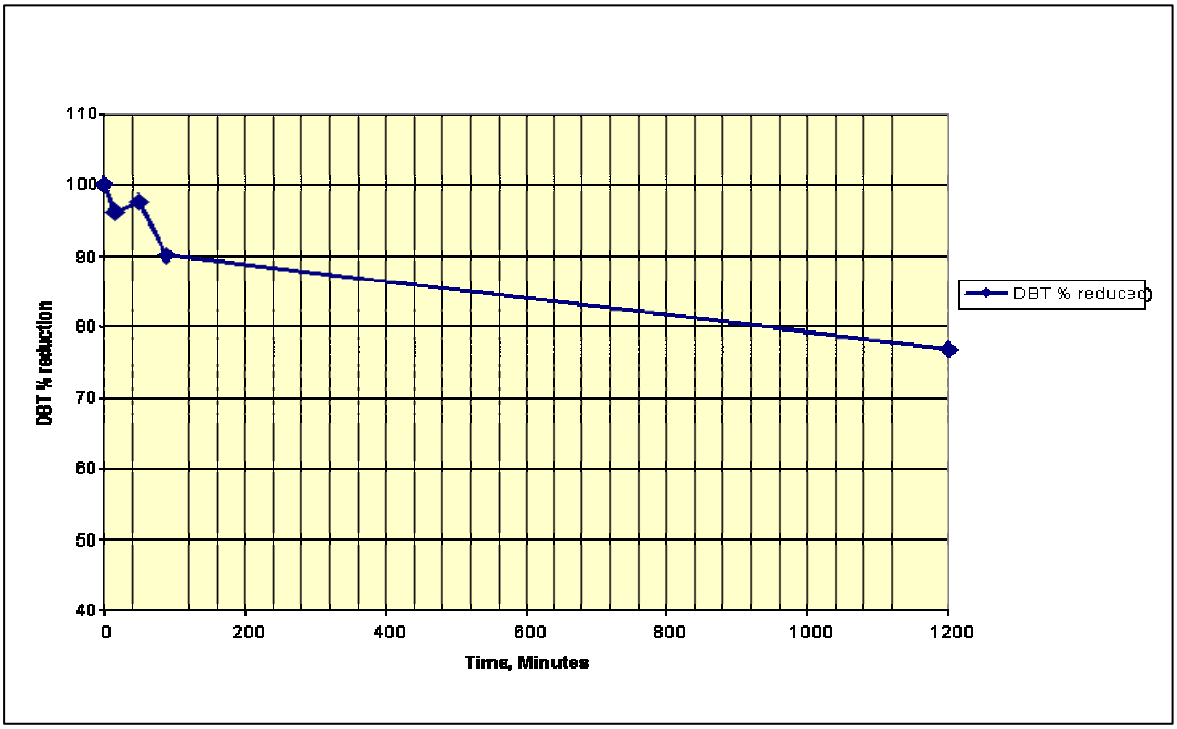


Figure 18. The effect of acetic acid on the oxidation of DBT at 50 ^{o}C and a longer period of time.

3.3.3 SOLVENT SELECTIVITY

It was not possible to study the selectivity of the solvent extraction on the model compound. As mentioned earlier the oxidation of the model compound resulted in a white precipitate that was completely soluble in different solvents such as methanol and acetonitrile. As a result, the mixture formed one layer that was difficult to separate. It is worth mentioning that the sulfone formed has very low solubility in water. The DBT sulfone stayed in the upper portion of the fuel part in its solid state when distilled water was added to the mixture after the oxidation. This observation proved that the water can not be used as claimed in some papers to separate the sulfones from the remaining hydrocarbons and the need for certain solvents became obvious. This observation directed this study to evaluate the solubilities of dibenzothiophenes and their sulfoxides and sulfone derivatives. The solubility of such compounds is an essential issue with respect to their extraction into aqueous reagents, solutions, and solvents, and their proper handling in the laboratory. The work presented here has indicated that alkyldibenzothiophenes have some moderate solubility in water, but the sulfones are quite insoluble. Table 7 shows some solubility and toxicity data for some of the mentioned sulfur compounds obtained from literature references [69,70].

Table 7. Solubilities of Dibenzothiophene, its alkyl derivatives and their Sulfoxides and Sulfones in water

Compound	Solubility mg/liter (1)	*LC_{50} mg/liter (2)
Benzothiophene	160	59
Benzothiophene Sulfone	540	14
3-Methyl Benzothiophene	49	2.6
3-Methyl Benzothiophene Sulfone	390	>390 (3)
5-Methyl Benzothiophene	46	14
5-Methyl Benzothiophene Sulfone	400	>400
Dibenzothiophene	1.0	>1.0 (3)
Dibenzothiophene Sulfoxide	320	20
Dibenzothiophene Sulfone	5.8	>5.8 (3)

*LC50 (lethal Concentration) values refer to the concentration of a chemical in air or water that can kill 50% of the test animals in a given time, usually four hours.

The oxidized hydrotreated diesel sample was used to relatively measure the efficiency of water, methanol and acetonitrile solvents extraction. The total sulfur found in all these experiments is shown in table 8. It clearly confirms the earlier contention that water is not effective in separating the sulfones from the remaining hydrocarbons. Methanol and acetonitrile show the same efficiency of sulfone extraction as described in graphs 19 and 20.

Table 8. Total sulfur after each separation process

Sample #1	Sulfur , PPM	Sample # 2	Sulfur, PPM
Before heating	6420	Before heating	6280
After heating	6780	After heating	6645
washing with water	6880	washing with Water	6275
washing with acetonitrile	3390	washing with methanol	4270

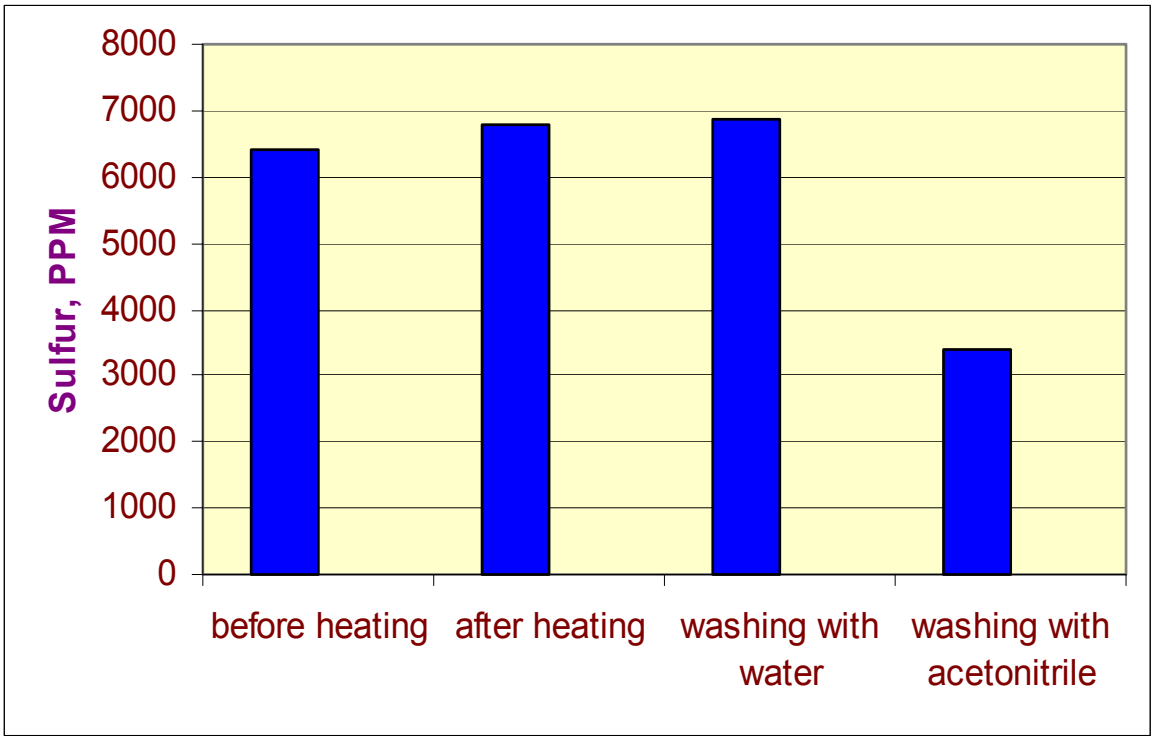


Figure 19. Total sulfur after oxidation and extraction with water and acetonitrile

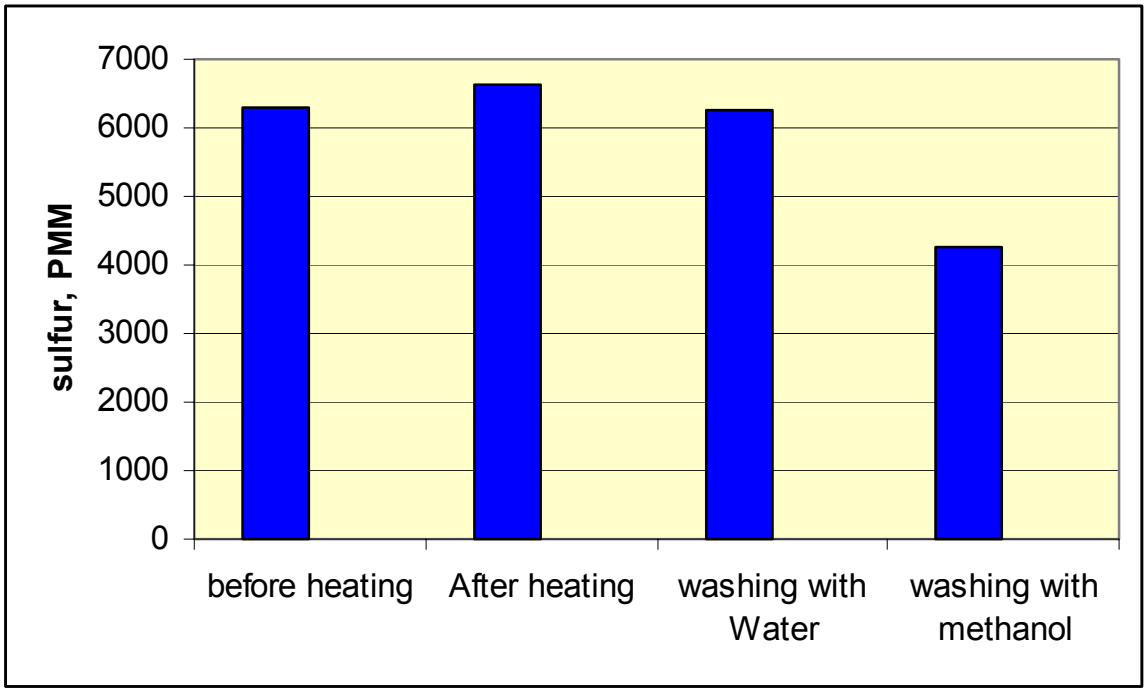


Figure 20. Total sulfur after oxidation and extraction with water and methanol

3.3.4 OLEFIN EFFECT

There was no oxidation of sulfur compounds during the experiment on the FCC gasoline (Figure 21). This directed the study to investigate the cause of such phenomena. Generally, the chemical compositions of gasoline and diesel are typical hydrocarbons except for the olefin content that exists in gasoline. It is well known that the FCC process produces gasoline with high olefin content. Therefore, it became necessary to evaluate the effect of olefin content in this study. 1-hexene was used instead of normal hexane in the model compound to study the olefin effect and compared to the model compound that contained no olefins.

The GC-MS spectra in figure 22 show the comparison of both results. In the presence of 1-hexene the oxidized DBT yield is significantly lower than the hexane sample.

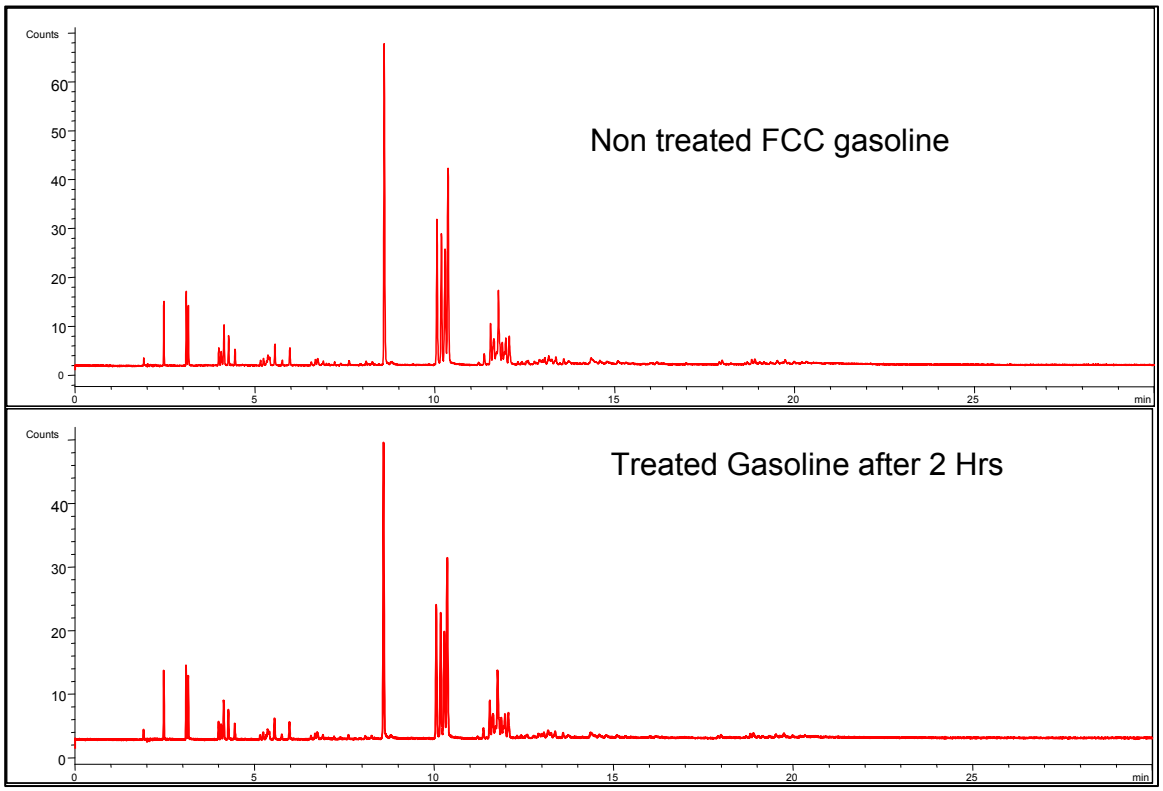


Figure 21. GC- AED spectra of FCC gasoline before and after oxidation.

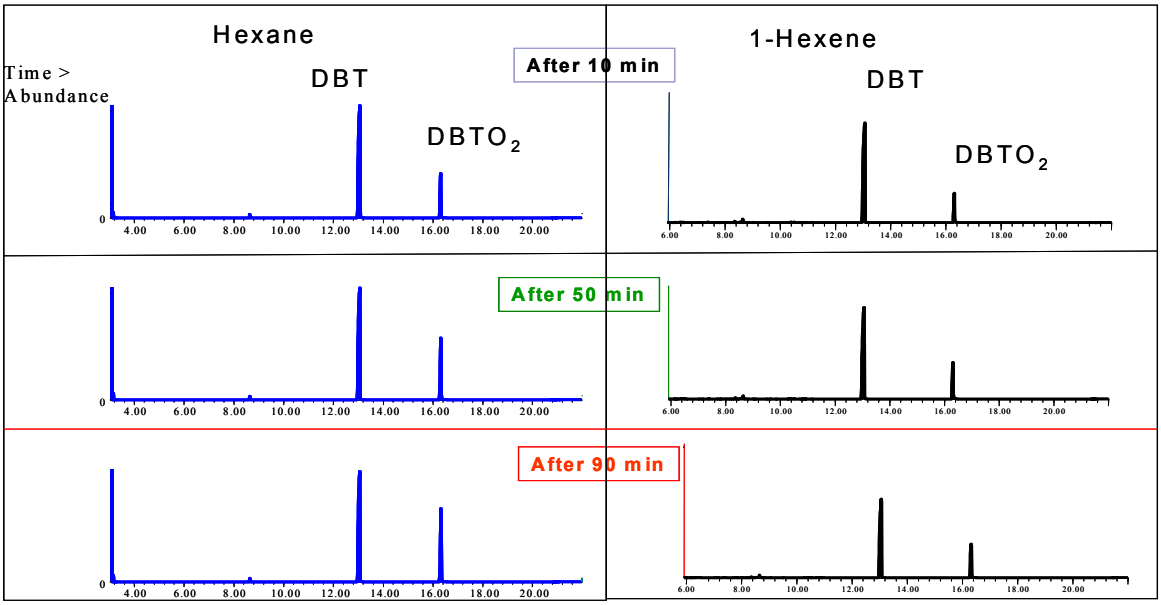


Figure 22. GC-MS spectra of DBT and oxidized DBT in Hexane and 1-Hexene at 50 °C

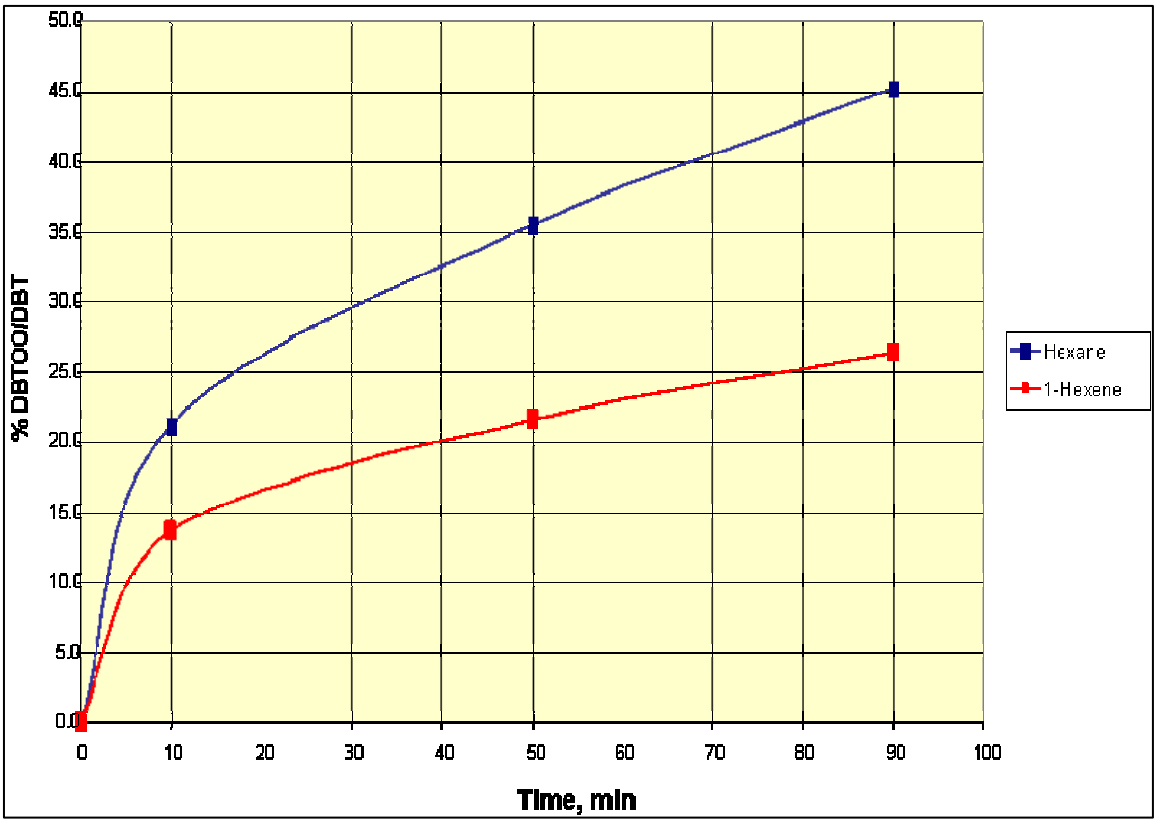


Figure 23. The percentage of oxidized DBT/DBT in presence of hexane and 1-hexene at 50 °C

It clearly shows that the olefin has some impact on the oxidation process. By analyzing the MS spectra of the products formed during both experiments, It was found that there was some epoxidation taking place in the presence of 1-hexene (figure 24). By reviewing the previous work on the epoxidation of olefins, it was reported that olefins could react with H_2O_2 in presence of acid to form epoxides [71,72]. In this experiment, there was some competing reaction between sulfur oxidation and olefin epoxidation as demonstrated by the graph in figure 24. This explains that the FCC gasoline, which has many types of olefins with total content reaching up to 45% in some refineries, can prevent the oxidation process.

Therefore, the oxidation/extraction methods for removing sulfur compounds in FCC gasoline require different approaches in order to perform deep desulfurization.

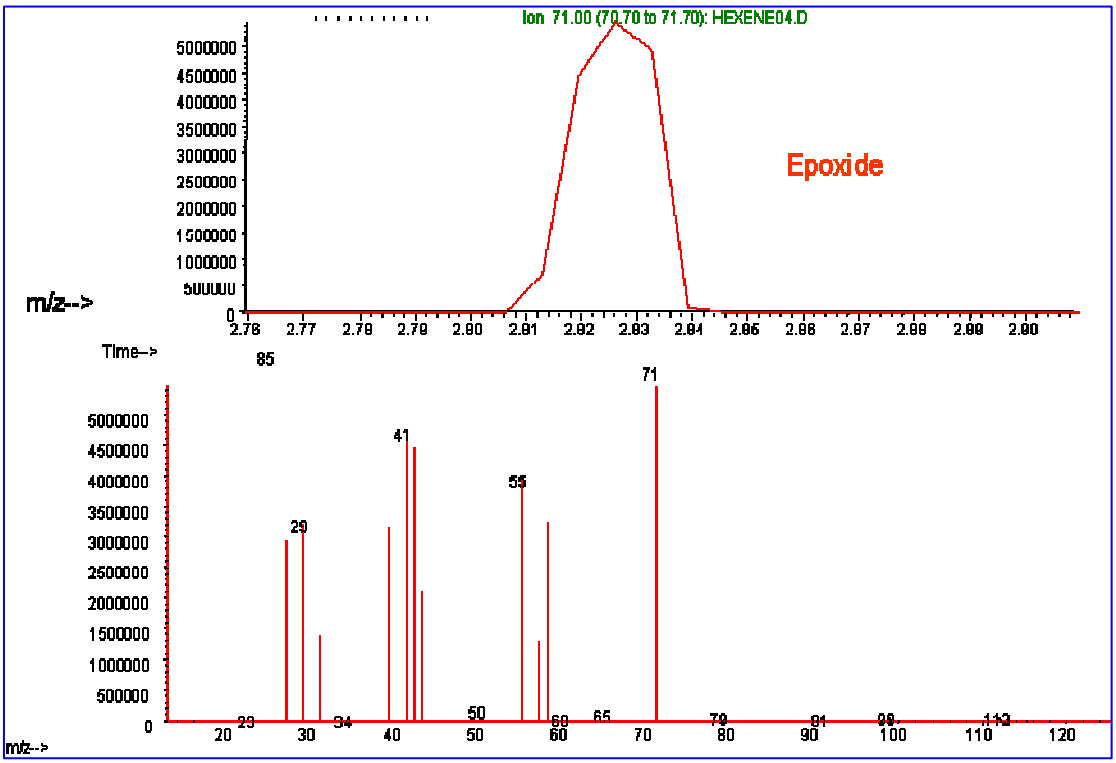


Figure 24. GC-MS spectrum of formation of epoxide during DBT oxidation in 1-hexene

3.3.5 METAL SALTS EFFECT ON THE OXIDATION OF DBT

There was no oxidation of DBT in the case of iron, cadmium salts and copper metal; however in cobalt acetate there was some oxidation of DBT, table 9 and figure 25. This is probably due to the decomposition of H_2O_2 that takes place when it contacts with salts.

Table 9. Formation of DBT-O and DBT-O_2 in presence of different metal salts.

	DBT-O_2% formation			
Time, minutes	$CdCl_2$	Co-acetate	$FeCl_3$	Cu
0	0	0	0	0
5	13.07	0	0	0
15	25.01	0	0	0
30	34.17	0	0	0
50	37.12	0	0	0
90	35.72	0	0	0

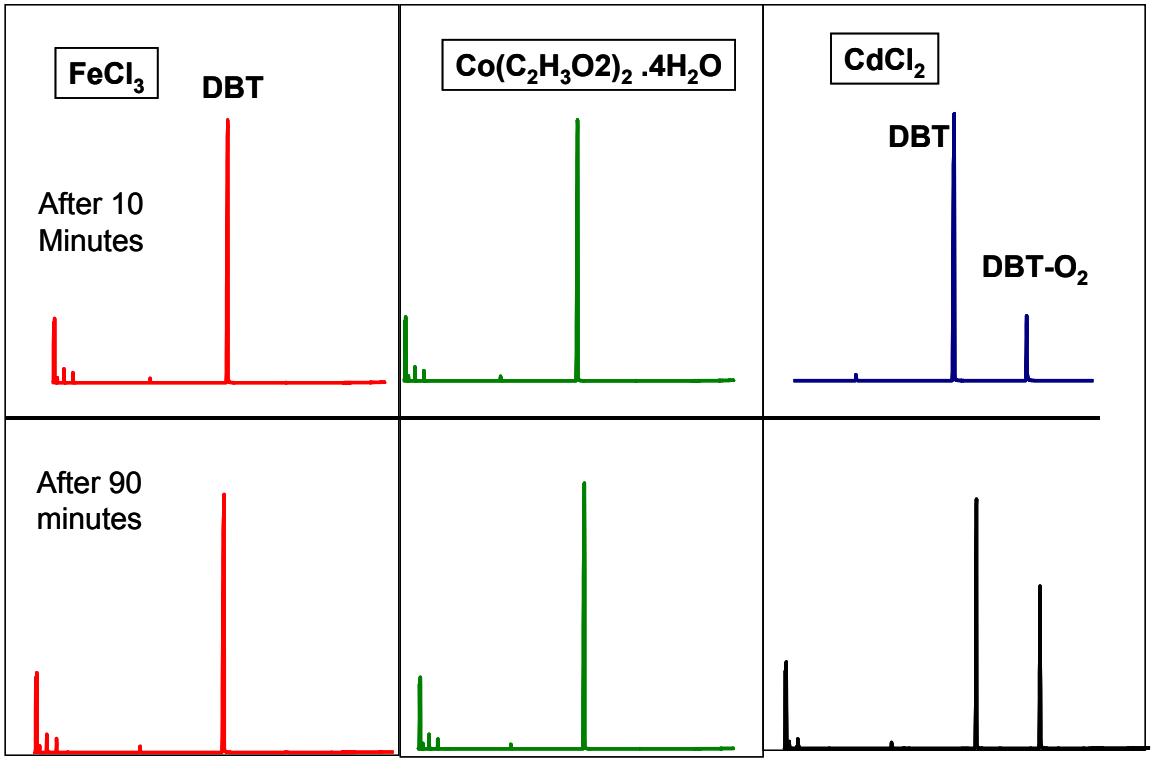


Figure 25. Oxidation of DBT in presence of different metal ions at 50 ºC

3.3.5 HYDROGEN PEROXIDE/FORMIC ACID MIXTURE CONCENTRATION EFFECT.

The aim of these experiments was to evaluate the effectiveness of oxidation/extraction in reducing the total sulfur. In this experiment the total sulfones extraction was used as an indicator of the H_2O_2 and formic acids concentration effect.

The results shown in the graph (figure 26) demonstrate that the sulfur was reduced to around 350ppm when reacted with 2.6% acid/H_2O_2. Higher concentrations did not have any impact on the sulfur content in the diesel sample. Although 1.3% of the acid/H_2O_2 mixture is chemically equivalent to the average mole ratio of the sulfur content in the hydrotreated samples, consideration needs to be given to the normal decomposition of H_2O_2 and other reactions that may take place with other aromatic hydrocarbons. From the graph (Figure 26), 2.6% acid/H_2O_2 was the optimum concentration to achieve oxidation which corresponded to double amount of the average sulfur compounds that were present in the diesel sample. The baseline sample with non-acid/H_2O_2 was used for the purpose of comparison. This sample was treated under the same conditions except with no acid/H_2O_2. The extraction results of all these samples are shown in table 10. The acetonitrile had some effect on the aromatic sulfur compounds even without any oxidation treatment. The total sulfur was reduced from 1022ppm to 846ppm after twice extraction with 10ml of acetonitrile. This highlighted the issue that acetonitrile could remove some sulfur compounds by direct extraction.

It is important to mention that the extraction efficiency is enhanced by the second acetonitrile extraction. This is due to the fact that during the first addition of

10ml of acetonitrile the diesel layer became a hazy cloudy mixture after one hour whereas in the second extraction the diesel layer became very clear. Therefore the sulfur value was obtained after the second extraction of acetonitrile to determine precisely the degree of sulfur removal.

Deep desulfurization was achieved by increasing H_2O_2/ formic acid concentration and heating the samples for a longer period of time (about two hours). Then, the sample was extracted twice with 1:1 ratio of acetonitrile to the diesel sample. The sulfur content in diesel layer was determined and found to be 176ppm and 41ppm after each extraction. Table 11 and graph 27 demonstrate such extraction.

Table 10. Effect of acid/H_2O_2 concentration on sulfones extraction

Original diesel sample	1022 PPM sulfur
Diesel sample before oxidation	After twice extraction with 10 ml of acetonitrile extraction
	846
Acid/H_2O_2 concentration, %	Sulfur PPM, after oxidation and twice extraction with 10 ml acetonitrile
1.3	823.3
2.6	361.0
3.9	373.7
5.2	334.4
6.5	366.1

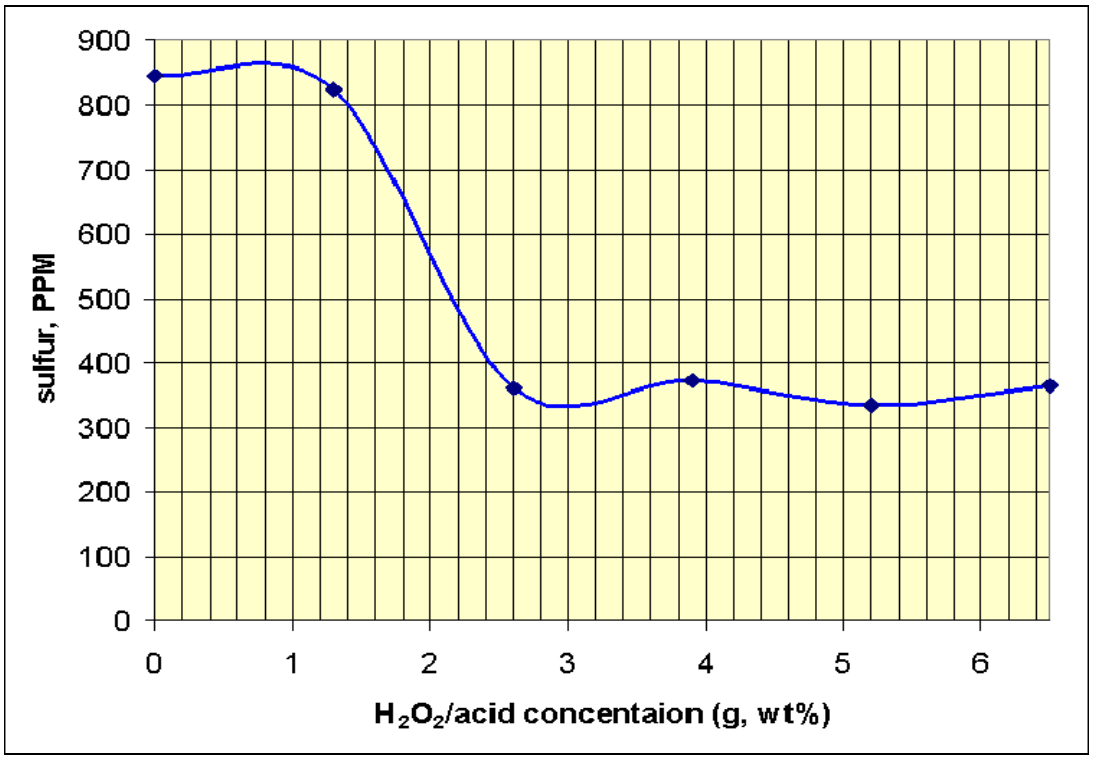


Figure 26. Extraction of sulfones after treatment of different concentrations of H_2O_2/formic acid

Table 11. Deep desulfurization of 50 ml of hydrotreated diesel sample.

Sample	Sulfur, PPM
Original sample, 50, ml	1052
1st wash with 50 ml of acetonitrile	176
2nd wash with 50 ml of acetonitrile	78
Acetonitrile portion	863

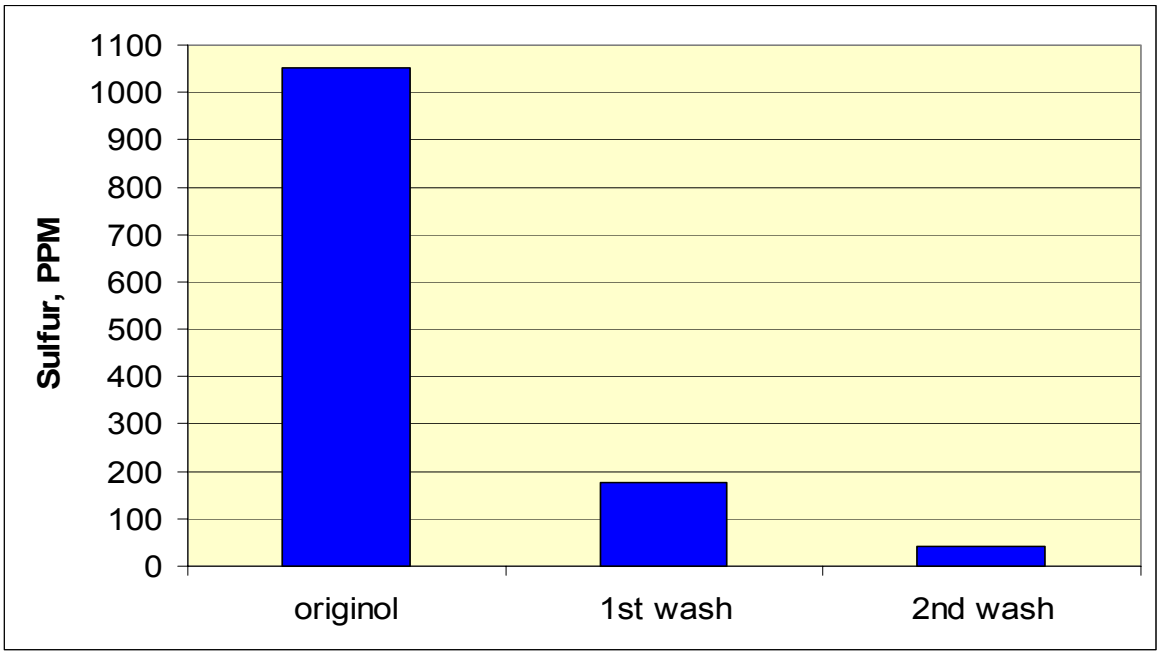


Figure 27. Total sulfur in diesel after oxidation and twice extraction with 50 ml acetonitrile.

3.4 OXIDATION OF FCC GASOLINE

The oxidation process using hydrogen peroxide and formic acid was not successfully accomplished on FCC gasoline figure 21. This cause was investigated under the olefin effect section. The most likely cause was due to the high olefin content. It is already known that some of the benzothiophene derivatives present in the diesel range can undergo oxidation to form their corresponding sulfones. Therefore it can be concluded that the olefins will have higher reactivity towards the epoxidation process than the oxidation reaction of the sulfur compounds.

3.5 Oxidation of hydrotreated diesel

Hydrotreated diesel was submitted to several experimental approaches to study the oxidation process. Some of these experiments have been explained in the previous sections such as solvent selectivity, acid/H_2O_2 concentration affect etc. The discussions here will focus on some of the important observations related to the sulfur oxidations process. From the DBT module, it was concluded that all hindered sulfur compounds can undergo the oxidation process to lead to the corresponding sulfoxide and sulfones (figure 28). In the presence of excess acid/H_2O_2, the reaction will go completely to the final sulfones products as has been observed in the model compound. This was confirmed by the GC-MS data (figure 14) where the mass fragmentation pattern of pure sulfone DBT-O_2 did not give any mass ions of 200. However, in the reaction of the DBT model compound with olefin and some diesel samples, it produced both products with mass ions of 200 and 216 that correspond to sulfoxide and sulfone, respectively. The incomplete reaction to sulfoxides and sulfones was due to the insufficient acid/H_2O_2 concentration or not enough time given to the reaction.

Another point worth mentioning here is the reactivity of different sulfur compounds in the diesel samples. Figure 29 shows the sulfur compounds in both original diesel and the treated sample. On closer inspection of the sulfur speciation of these samples in terms of their peaks heights, the following observations can be drawn: The reactivity of sulfur compounds depends on the position of alkyl groups on the DBT. The peaks of C_4DBT, C_3DBT, C_4BT, C_3BT almost disappeared, while the peaks of C_1BT, C_2BT, DBT, C_1DBT, C_2DBT compounds did not react completely. This can be explained by the reactivity of the sulfur DBT as a result of

the electron density of the alkyl group contributions. As for the proposed mechanism of the sulfide oxidation reaction described in section 2.1, the first step of the reaction depends on attacking the hydrogen peroxide by the sulfur atom. Therefore the higher electron density as a result of donating electron groups will play a significant role on the rate of the oxidation reaction. In addition, the position of alkyl groups and the chain length would also have some effect on the electron density of DBTs, which has already been reported [30].

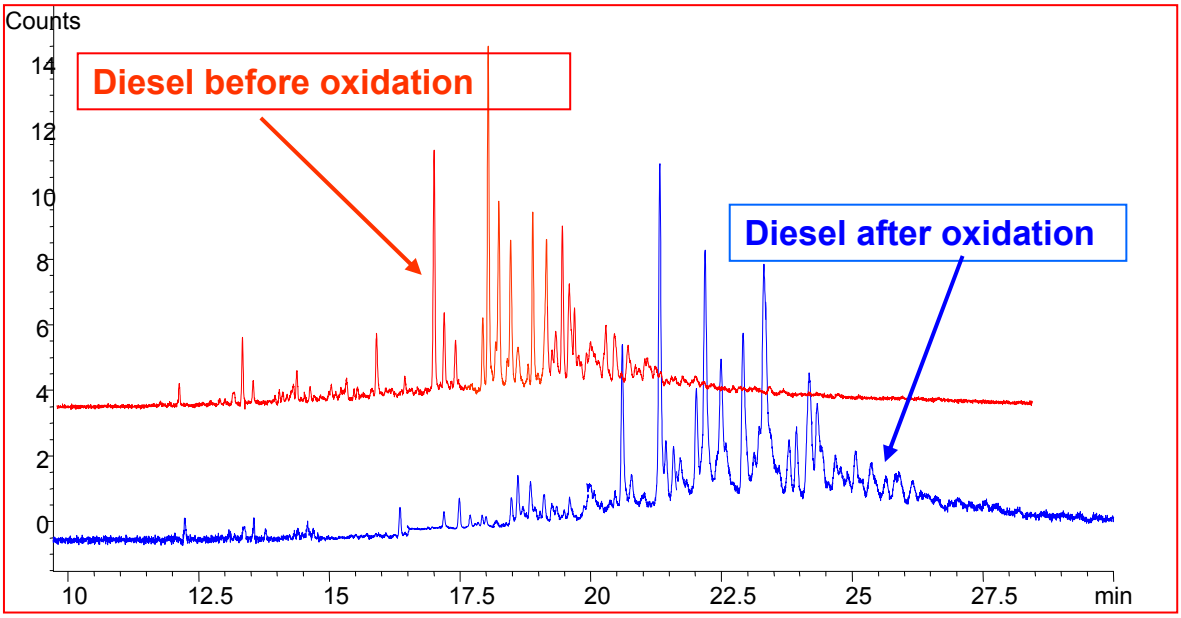


Figure 28. GC-AED Spectra of diesel before and after oxidation.

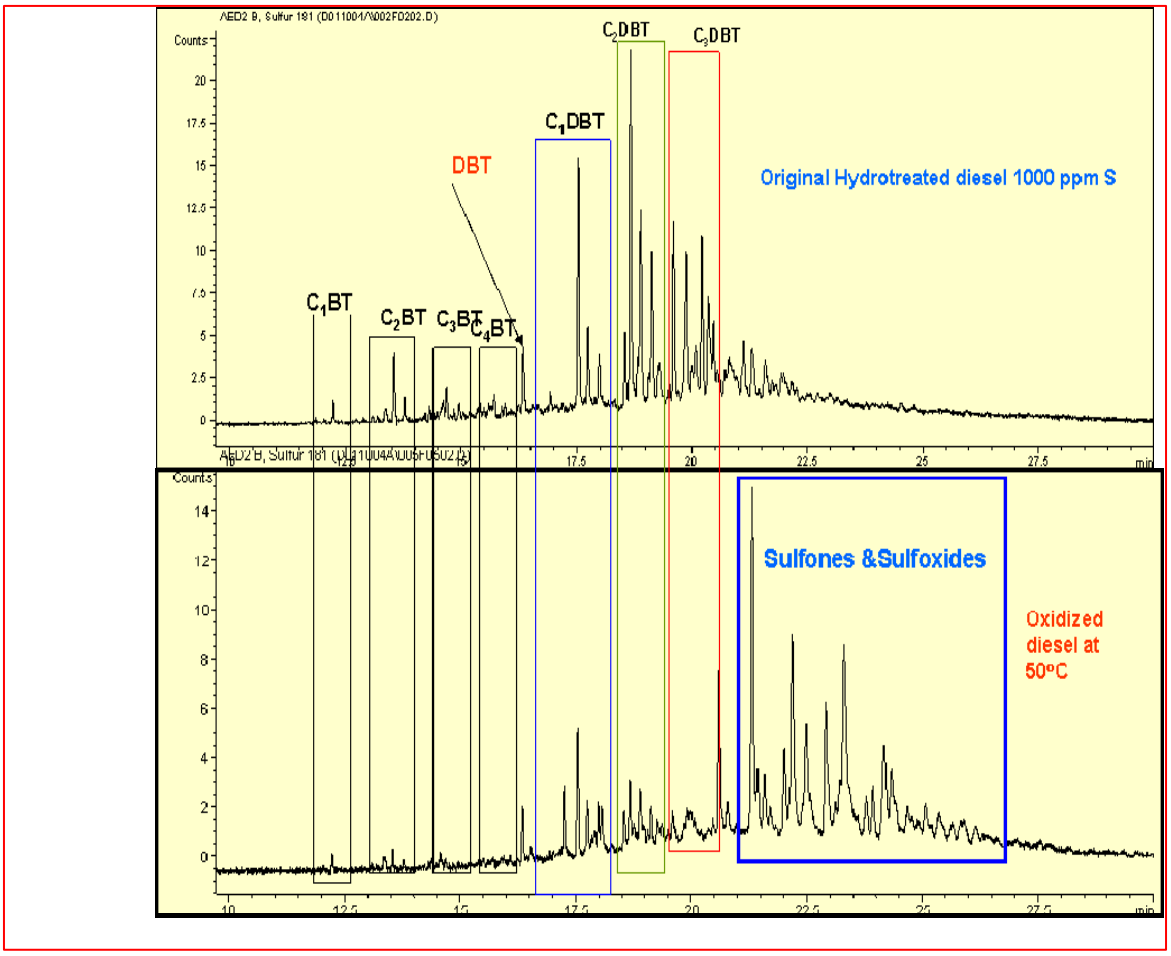


Figure 29. Sulfur compounds in diesel before and after oxidation

3.6 Sulfones speciation separated from diesel after oxidation.

GC-AED chromatograms of the diesel, oxidized diesel, and extracted diesel appear in figure 30 which also indicates the sulfur removal of these compounds after first and second extraction with acetonitrile. Selected ion mass chromatograms appear in figure 31.

Mass spectrometry was used to characterize the components in the range 20-600 amu. Ions pertaining to calculated sulfones moieties were extracted for convenience. Mass spectra are also depicted for verification. Assignment of sulfone molecules is also performed and displayed on top of each spectrum. It

has to be noted that there are coelutions of sulfone homologies in many instances and these are marked where applicable by a solid arrow heading toward the molecular ion of the sulfones molecule. Figures 32 demonstrates some of these compounds and figures 33 &34 show examples of the extracted ion for two of these compounds. Appendix I includes the remaining GC-MS extracted ions for all these sulfones. These compounds are shown in table 12 according to their retention time and mass.

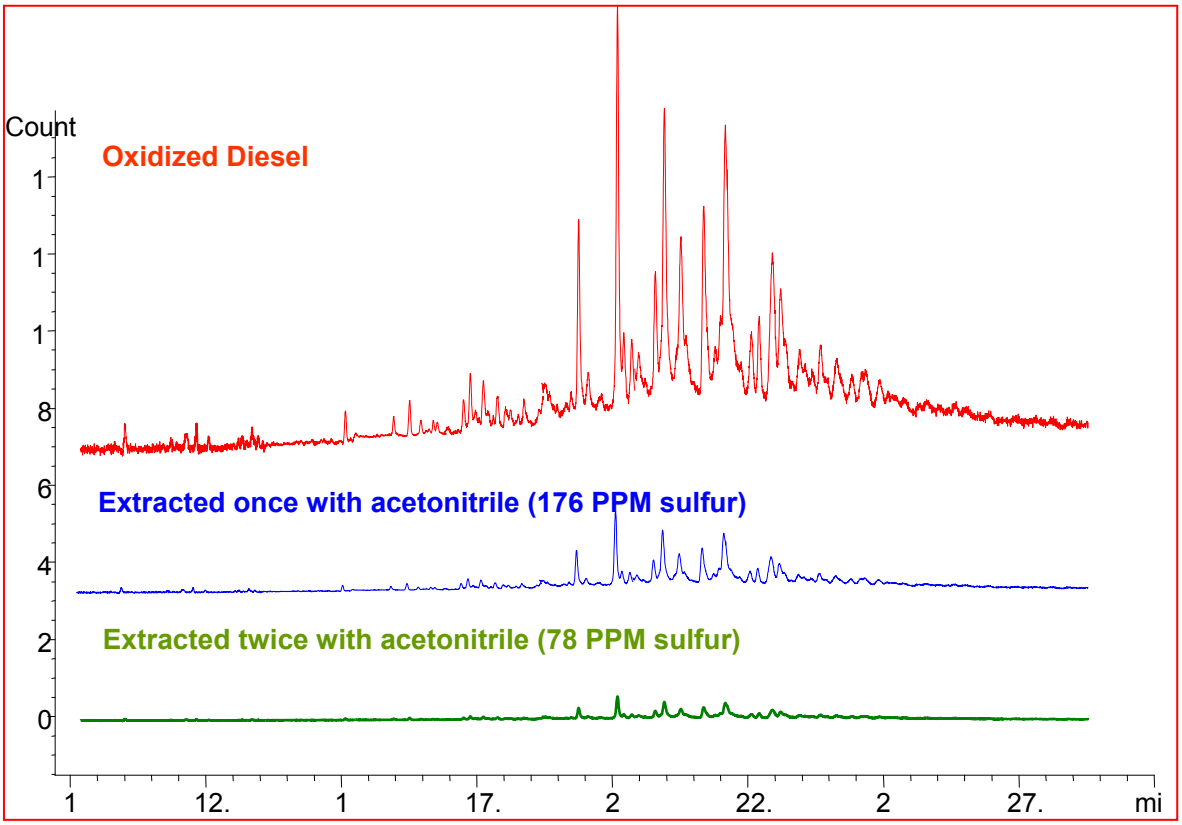


Figure 30. GC-AED Chromatograms of Oxidized diesel and extracts

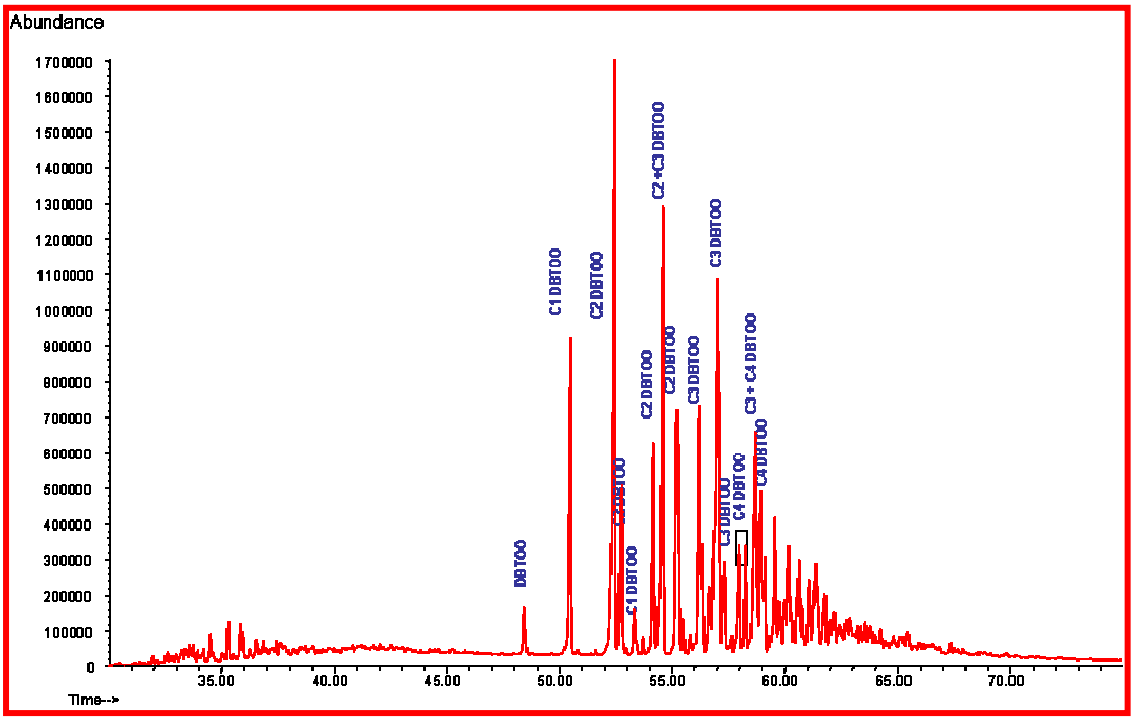


Figure 31. GC-MS spectra of sulfones

Table 12. Sulfone speciation in hydrotreated diesel

R.T	Mass	Name
48.42	216	DBTO2
50.435	230	C_1DBTO_2
52.228	230+244	C1+C2DBTO2
52.406	244	C2DBTO2
52.695	230+244	C1+C2DBTO2
53.338	230	C1DBTO_2
54.488	244+258	C2+C3DBTO2
54.514	244+258	C2+C3DBTO2
55.158	244+258	C2+C3DBTO2
55.189	258	C3DBTO2
55.453	244+272	C2+C4DBTO2
55.467	244+272	C2+C4DBTO2
56.583	258+272	C3+C4+DBTO2
56.846	244+272	C2+C4DBTO2
56.912	244+258+272	C2+C3+C4DBTO2
57.989	272	C4DBTO2
58.206	258+272	C3+C4DBTO2
58.705	258+272	C3+C4+DBTO2
58.895	272	C4DBTO2
58.941	272	C4DBTO2
59.02	258+272	C3+C4+DBTO2
59.033	258+272	C3+C4+DBTO2
59.513	272+286	C4+C5 DBTO2
59.559	244+258+272+286	C2+C3+C4+C5DBTO2
59.66	244+258+272+287	C2+C3+C4+C5DBTO2
60.117	258+272+286	C2+C4+C5 DBTO2
60.163	258+272+286	C2+C4+C5 DBTO2
60.617	272+286	C4+C5DBTO2
60.761	258+272+286+300	C2+C4+C5+C6 DBTO2
61.017	244+258+272+286+300	C2+C3+C4+C5+C6DBTO2
61.333	244+258+272+286+300	C2+C3+C4+C5+C6DBTO2
61.424	272+286	C4+C5DBTO2
62.902	258+272+286+300	C3+C4+C5+C6DBTO2

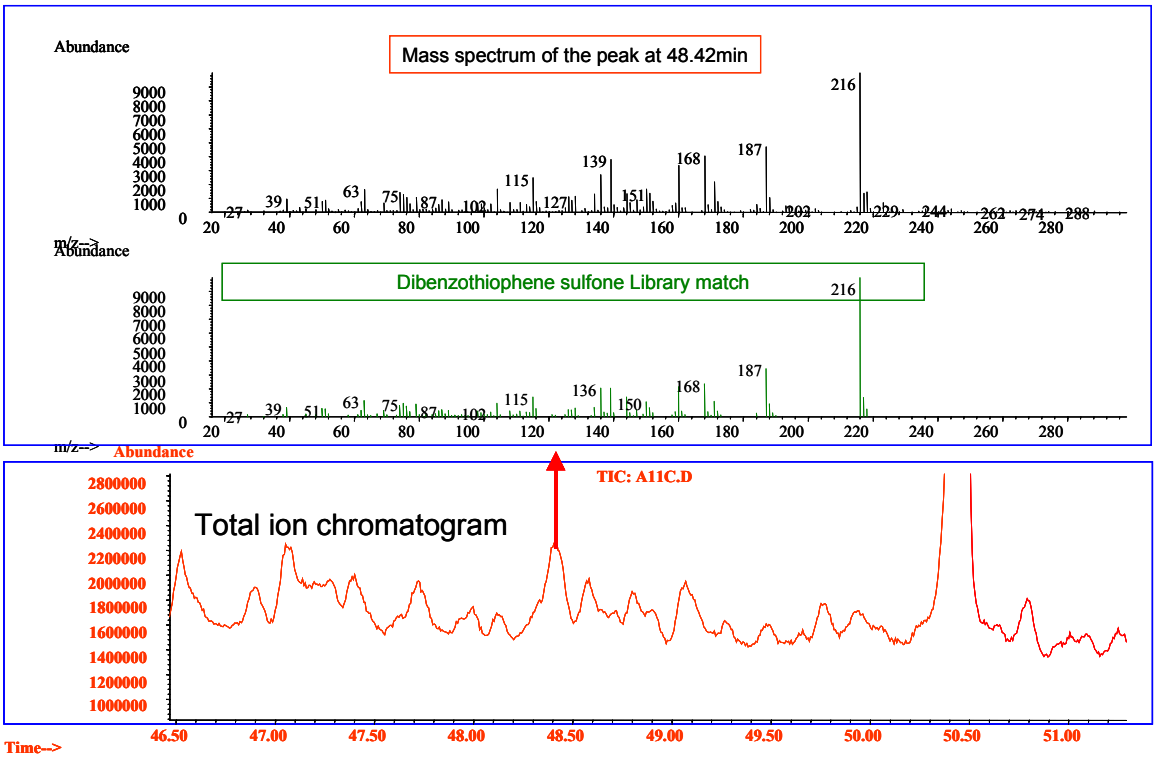


Figure 32. GC-MS spectra of extracted ion for DBT-O_2 and library spectra match

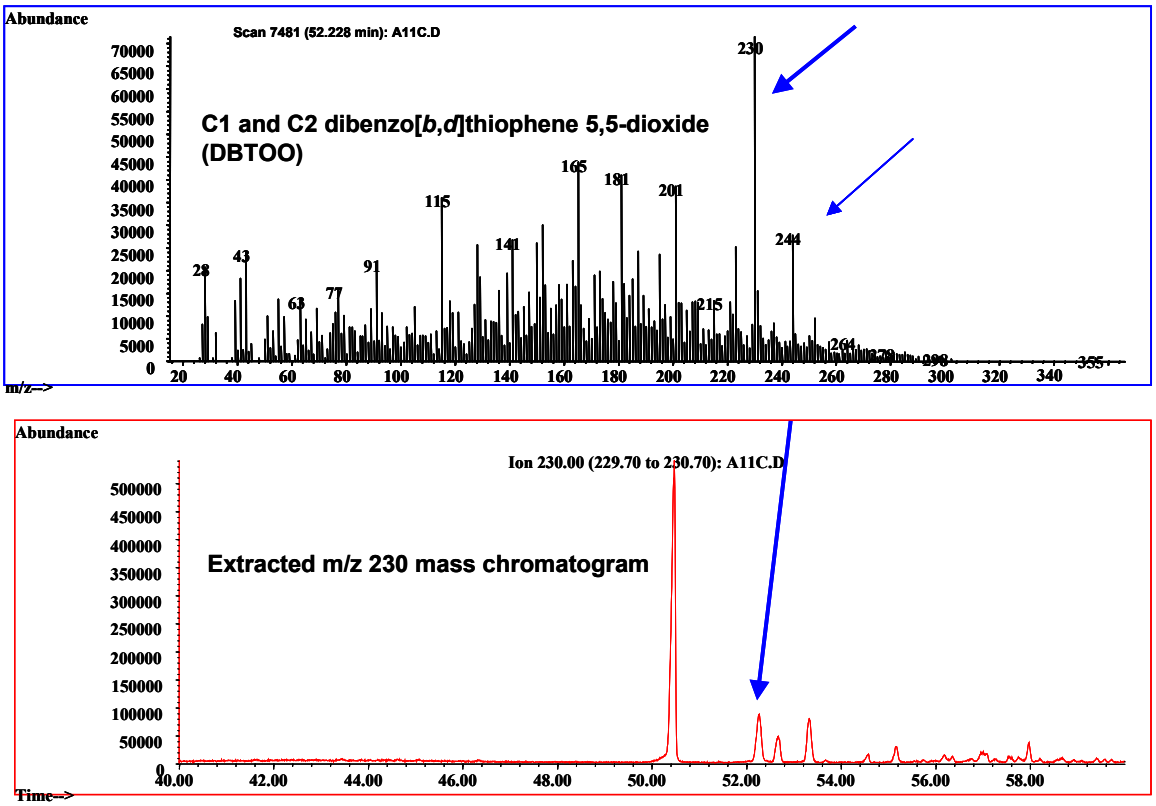


Figure 33. GC-MS spectra of extracted ions for C_1&C_2 DBT-O_2

It is worth noting that this is the first time that GC-MS of sulfones is reported in such detail. The mass spectra were used to identify these peaks. No library compounds are available for comparison purpose; however the result from the model compound DBT-O_2, discussed earlier, was used as a key to identify some of these compounds. The mass of the oxidized DBT has resulted in the following named compound, dibenzo[b,d]thiophene 5,5-dioxide with total mass of 216.03 represented in the following formula $C_{12}H_8SO_2$. From the previous work and the results of this study, it became clear that most of the untreated sulfur compounds are thiophinic hindered types which mainly exist in this case of the hydrotreated diesel. It is also known that during the oxidation process the sulfur compounds that undergo this process can be separated from the remaining part of the fuel. By knowing this, it may be concluded that the only groups that will contribute to the total mass of the resulting sulfones are those with attached alkyl groups which already exist in the original sulfur compounds. Therefore, the scanning of certain mass that represents the methyl molecular mass and their multiple mass will give various isomers of the sulfones products.

Fragment ions appearing in selected ion chromatograms corresponding with the elution times of heavier molecules arise from the loss of methyl groups (-15 mass) from the P+1 isotopes which have approximately 10% abundance relative to the parent ion. Table 12 demonstrates the possible sulfones compounds that resulted from the oxidation of hydrotreated diesel. Such an approach can be used to identify more sulfur compounds that exist in the whole diesel or even in the high boiling range fractions of crude oil. Although the acetonitrile portion was washed twice with normal hexane, the samples showed some remaining aromatic

hydrocarbons as shown by GC-MS result (figure 33).

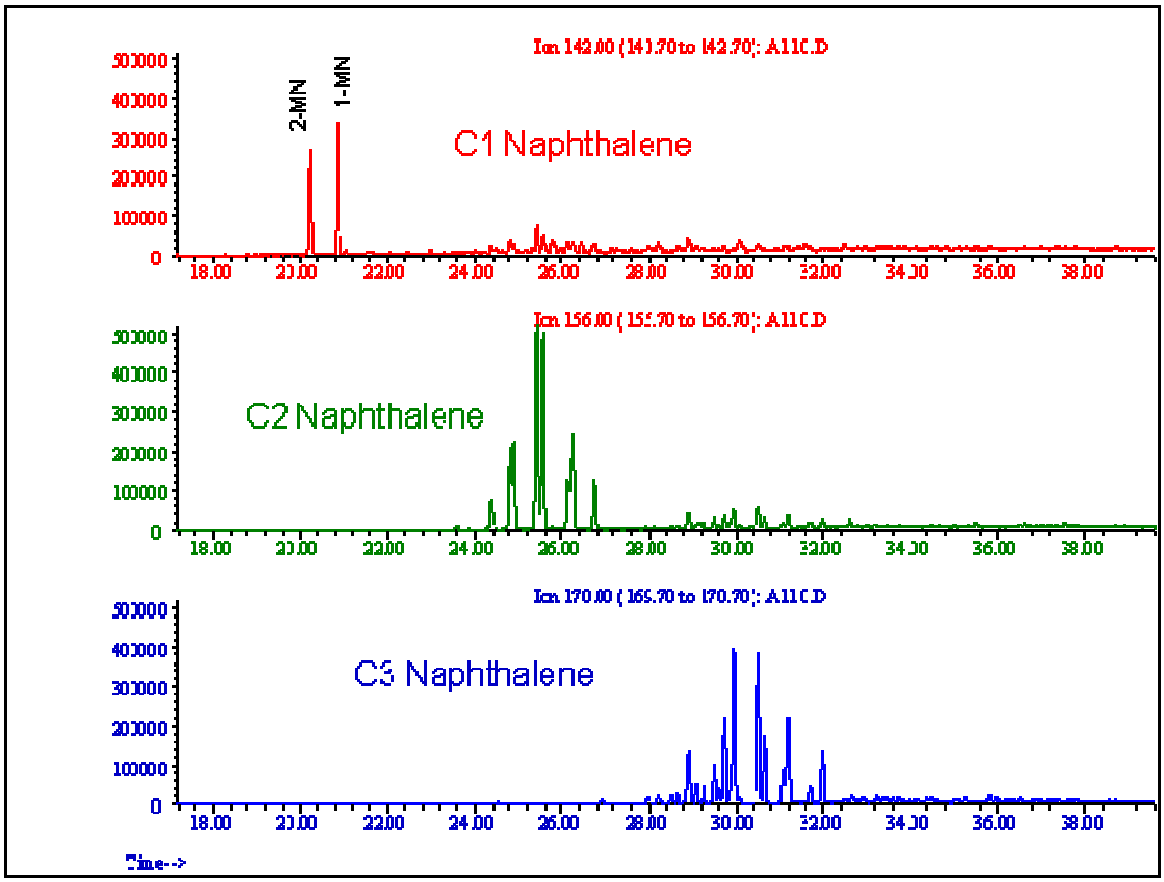


Figure. 34. GC-MS spectra of detected naphthalenes in the Sulfone portion

CHAPTER 4

THE EFFECT OF ACETONITRILE EXTRACTION IN DIESEL QUALITY

This experiment was conducted to study the effect of direct acetonitrile extraction on the quality of diesel in terms of quantity lost. The diesel sample was submitted to direct acetonitrile extraction without any oxidation. The GC-MS data (figure 34) confirmed that some aromatic hydrocarbons were removed along with sulfones during the acetonitrile extraction. The results of these experiments revealed some useful information about the extraction process. First, the experiment with 10ml acetonitrile required overnight to produce a better separation. The volume of this experiment after one hour showed that there was about 0.5ml of acetonitrile remaining in the diesel layer; while overnight 0.5ml of diesel was found in the acetonitrile portion. The experiments using 20ml and 50ml of acetonitrile gave the same results after one hour and overnight. This probably has to do with the solubility and phase separation of different hydrocarbons in diesel which may depend on the volume ratio of solvent to solute. The smaller the ratio of acetonitrile to the diesel the more difficult and longer time is required to achieve a good separation. However a greater volume of acetonitrile means a higher cost in terms of the extraction and recovery process. In addition the quantity of diesel lost increases with increasing volume of acetonitrile. Table 13 and figure 35 summarize the results of these experiments. The acetonitrile alone has a great effect on sulfur removal without any pretreatment process. The sulfur content was reduced from its original value of about 1041ppm to about 563ppm after the second extraction of 50ml of acetonitrile. Table 14 and figure 36

demonstrate such an effect.

Figure 37 demonstrates the effect of acetonitrile extraction on diesel with and without an oxidation process. Direct extraction resulted in some sulfur removal in addition to other aromatic hydrocarbon species. This is probably due to the small polarity differences between the sulfur-containing compounds and other aromatic hydrocarbons. The oxidation of sulfur compounds resulted in the formation of sulfoxides and sulfones products that are relatively polar compared to the original sulfur species. This gives preference to sulfur compounds to be easily separated with minimum impact on removing other aromatic hydrocarbons.

Table 13. The effect of acetonitrile extraction in diesel quality

After one hour					
Diesel, ml	Acetonitrile, added (ml)	Diesel, recovered ml	Acetonitrile, recovered, ml	Diesel lost, ml	Diesel lost%
50	10	50.5	9.5	-0.5	-1
50	20	49	21	1	2
50	50	48	52	2	4
Overnight					
Diesel, ml	Acetonitrile, added (ml)	Diesel recovered ml	Acetonitrile, recovered, ml	diesel lost, ml	Diesel lost%
50	10	50.5	9.5	0.5	1
50	20	49	21	1	2
50	50	48	52	2	4

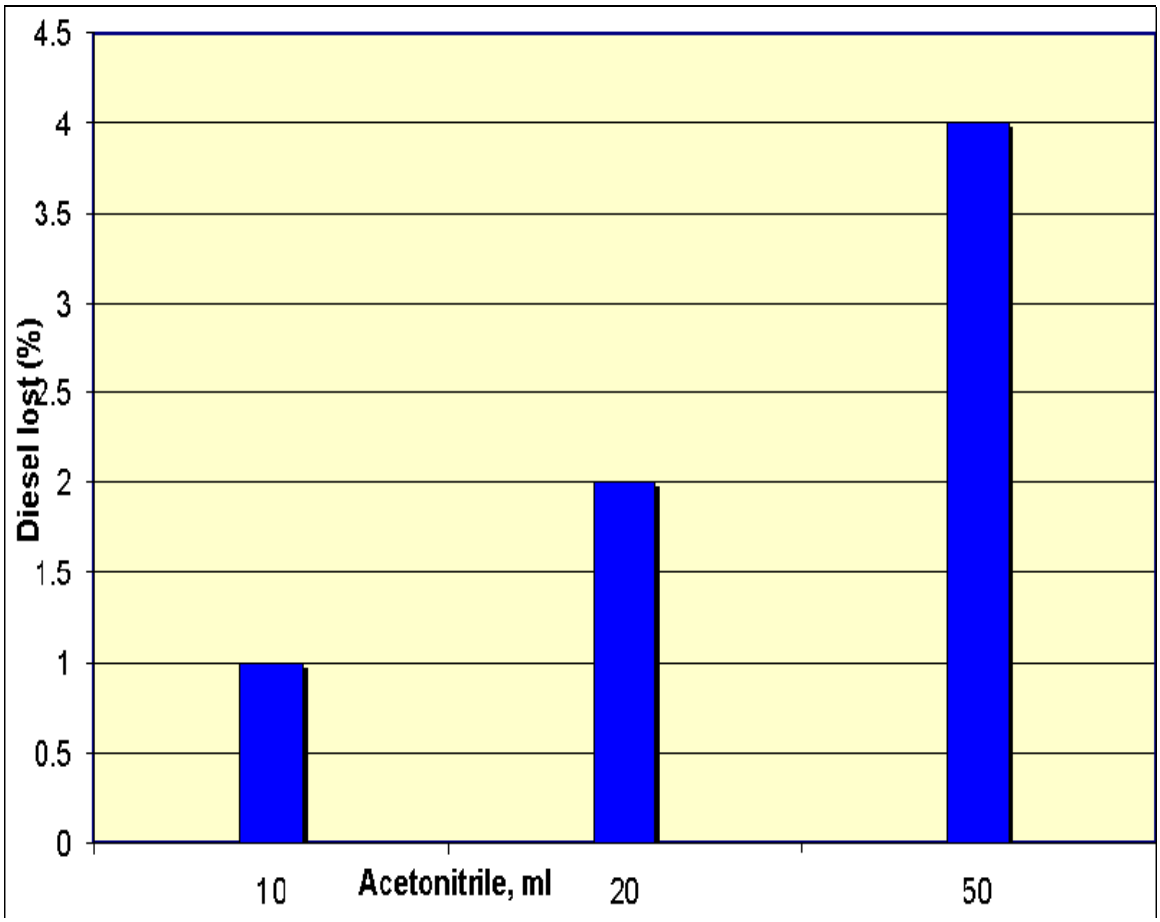


Figure 35. Impact of direct acetonitrile extraction on diesel quality

Table 14. The effect of direct acetonitrile extraction on sulfur removal

	Sulfur content, PPM	
Amount of acetonitrile	1st extraction	2nd extraction
0	1041	1041
10	902	801
20	858	738
50	714	563

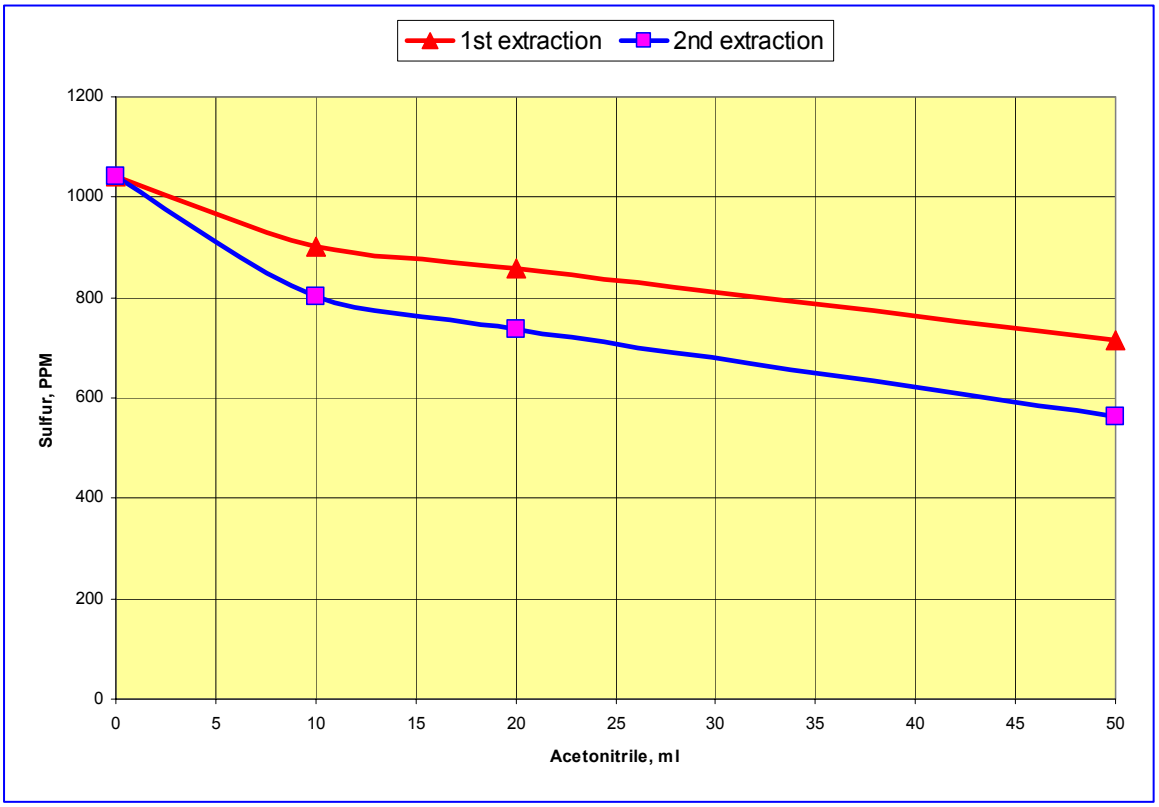


Figure 36. The effect of direct acetonitrile extraction on sulfur removal

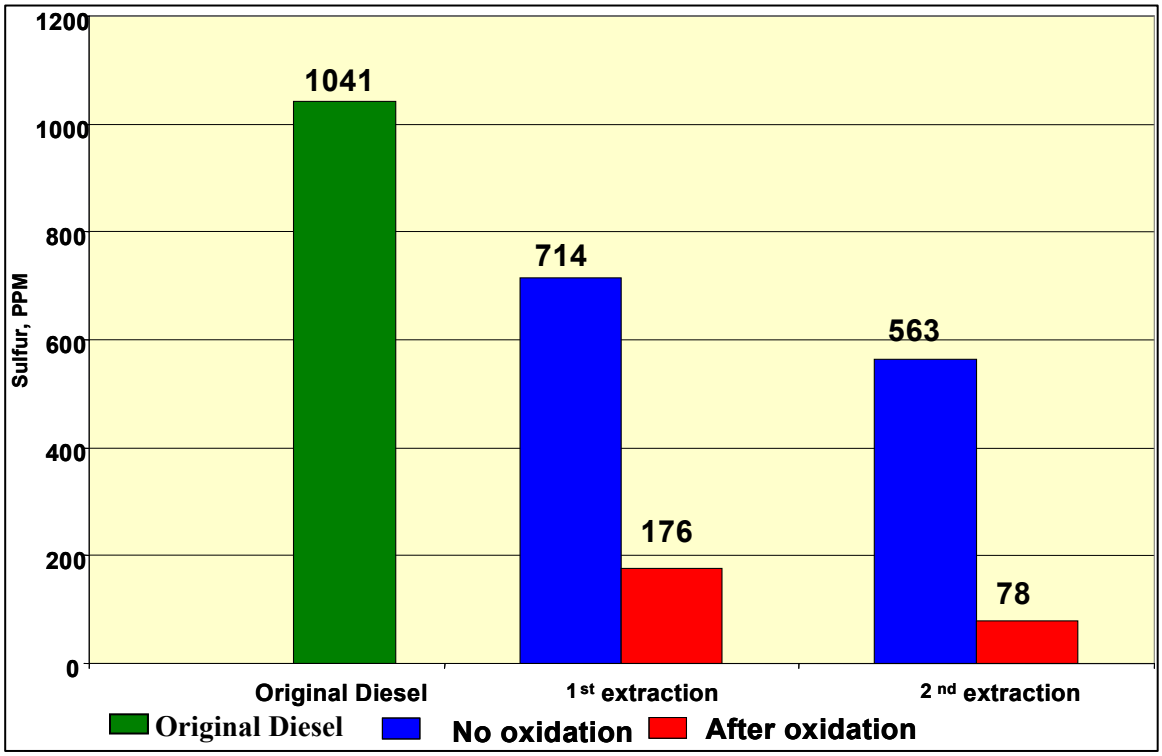


Figure 37. Effect of acetonitrile extraction on sulfur removal, with and without Oxidation

CHAPTER 5

DEEP DESULFURIZATION USING METAL IONS

Several mono and bi-metal salts with different ligands have been tested to physically adsorb and separate sulfur compounds. The purpose of this work is to remove the hindered compounds by reacting the thiophinic compounds with metal salts to be able to separate them physically by extraction. This method is considered to be the most cost effective approach to deep desulfurization. The model compound used comprises of DBT, hexane, and toluene.

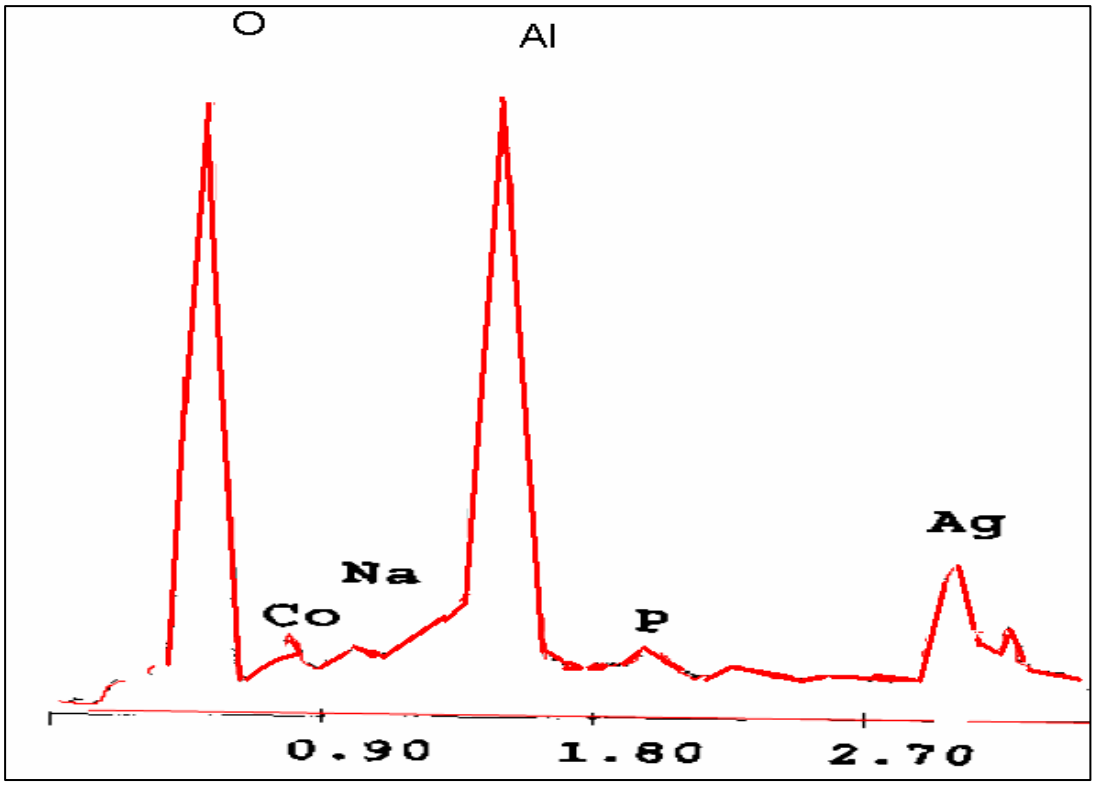
No sulfur detection was observed in all the samples from the experiments indicating that such complex formation is not possible under the experimental conditions. Angelici at,Iowa State University, Department of Chemistry has been working for the last few years in developing a catalyst that is able to react with sulfur thiophinic compounds using Ru (II) in the form of $Ru(NH_3)_5(OH_2)^{2+}$. He indicated that some reactions have been accomplished under certain conditions, however the practicality of such an approach needs further investigation. This is probably due to the instability of complex formation with thiophinic hindered compounds in the very complicated mixture of hydrocarbons compounds that exist in such fuel.

In addition, the hindered sulfur compounds remained untouched in the hydrodesulfurization process after severe reaction conditions. This indicates that adsorption with catalyst via electron pairs of the sulfur atom is very difficult even at high temperature and pressure. It seems that designing a catalyst for physical

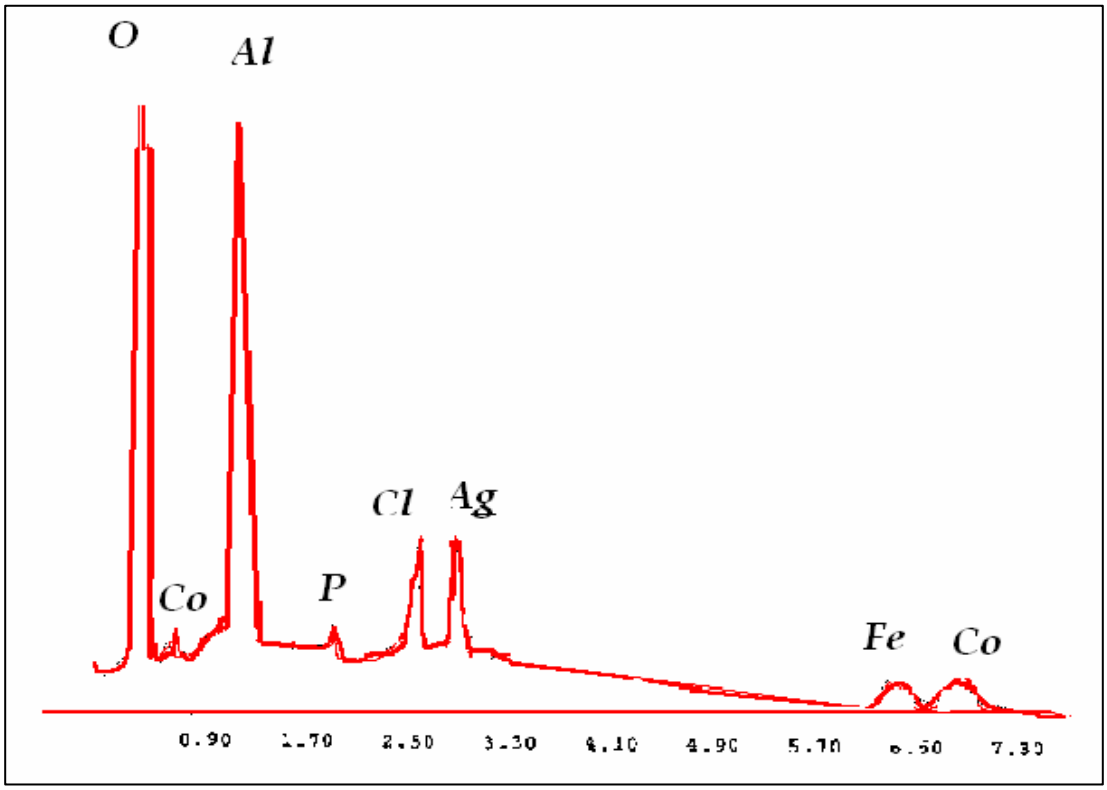
separation of such hindered sulfur compounds is a very challenging task, especially with competition of other hydrocarbons that exist in the fuel such as, other heteroatoms organic compounds, aromatic hydrocarbons etc. Table 15 and figures 38 & 39 below summarize the various metals salts and ligands used in this work.

Table 15. different metals and ligands used

Metals salt	**Ligands**		
Mono metals	**Water**	**EDTA**	**NH3**
Copper chloride Cobalt acetate Ferric chloride Ru Chloride	X	X	X
Cobalt Acetate + Copper Chloride	X	X	X
Ferric Chloride + Cobalt Acetate	X	X	X
Chloride + Copper Chloride	X	X	X



Figurer 38. ESEM for cobalt chloride



Figurer 39. ESEM for cobalt and ferric chlorides

CHAPTER 6

SUMMARY AND RECOMMENDATIONS

The oxidation extraction technique was found to be a promising approach for the reduction of sulfur to less than 100ppm from the original value of 1044ppm, with total removal of 92%. This was achieved at low temperature, 50ºC and atmospheric pressure. The direct extraction of diesel fuel without any oxidation has resulted in about 45% sulfur removal, however such direct extraction has a great impact on removing significant amount of other aromatic hydrocarbons species. The oxidation extraction technique is not applicable to FCC gasoline due to the high olefin content that tends to react with hydrogen peroxide to form epoxide products.

The new approach of identifying the sulfones produced, which is based on GC-MS technique will play an important role in the future to help identify more sulfur compounds in different petroleum products. The sulfones identified can be included in the GC-MS database as good references for future studies. The technique basically depends on oxidation of fuels in presence of excess H_2O_2 for sufficient time. Then, the oxidized products are separated and submitted to GC-MS for sulfur identification using selected mass ions.

The metals ion-sulfur complexation was found to be unsuitable to physically separate the hindered sulfur compounds. This is probably due to the instability of such a complex. However, this piece of work has provided more knowledge to assist in adopting a different approach in the future using such a technique.

In summary, the study recommends that the oxidation extraction technique be used as an additional process to the hydrodesulfurization to enable the refiners to meet the future environmental sulfur regulations. Conventional hydrodesulfurization can be used to lower the sulfur content to few hundreds ppm sulfur. Then, the oxidation/extraction approach needs to be used to go for ultra-deep desulfurization as it may provide better mean and cost effective way in order to meet the future sulfur environmental requirements.